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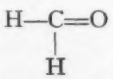
Formaldehyde in the Treatment of Textile Materials

By A. J. HALL, B.Sc., F.I.C., F.T.I.

FORMALDEHYDE, a very pungent gas which can be most conveniently handled as a 40% solution in water, has been used in comparatively small amounts in the treatment of textile materials during the past twenty years, but more recently it promises to become of considerably greater importance. On the one hand it has been found essential to the Tootal anti-crease process which is likely to be widely applied to many types of cotton and rayon goods, and on the other, recent investigations indicate that formaldehyde can enter into combination with cellulose to form a methylene ether thereby giving the fiber peculiar physical and chemical properties capable of being utilized in dyeing and finishing processes such as are used for yarns and fabrics. These new uses for formaldehyde are worthy of consideration.

At the present time there is a great opportunity to secure increased business in the processing of textile materials by conferring new useful effects on yarns and fabrics. The purchasing public is certain to be attracted by a fabric which has a more attractive appearance as regards color or luster, a softer handle, or greater durability. Such effects can only be produced by chemical modification of the fiber. In this article attention is drawn to the possibilities of chemically combining cellulose fibers (cotton and viscose rayon) with formaldehyde, and an account of researches along these lines is reviewed.

Formaldehyde is an extremely reactive substance having the composition indicated by the following structural formula:

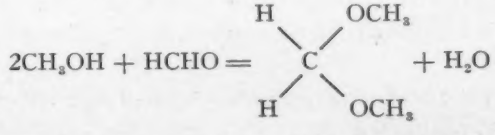


This formula suggests that it can react both as an aldehyde and also as a ketone, both of these types of substances being well know to be very reactive and capable of entering into combination with a wide variety of compounds. It is not therefore surprising that formaldehyde is able, under suitable conditions, to unite chemically with cellulose.

In the past, the textile uses of formaldehyde have been mainly restricted to its application to wool for the purpose of giving it increased resistance to alkalis and to sulfur dyes (in the dyeing of sulfur colors on cotton-wool union goods), and its use as an after-treatment on cotton and viscose goods dyed with direct dyes since formaldehyde is able to combine with certain of these dyes and thereby increase their fastness to washing. It may be usefully pointed out that a very fast and pleasing black shade on viscose rayon hose and knitted goods can be produced by first dyeing with Formal Fast Black G or R and then treating for a few minutes in a warm dilute solution of formaldehyde. Also, more recently it has been suggested that formaldehyde can be employed for softening cellulose acetate rayon goods since it is found to have a mild swelling action on this type of rayon.

The above uses are not likely to achieve anything more than the improvement of standardized dyeings and finishes, and it is therefore to the new uses that one turns for more far-reaching developments.

Considering first the manner in which formaldehyde can combine with cellulose, it must be remembered that cotton and viscose rayon fibers consist entirely of cellulose the molecule of which contains three hydroxyl groups. Formaldehyde combines with an hydroxy substance (methyl alcohol is used as an illustration since it is the simplest of hydroxy compounds) thus:—



In much the same manner it would be expected that formaldehyde would combine with cellulose—

$$C_6H_7O_2(OH_3 + HCHO = C_6H_7O_2(OH) \begin{matrix} O \\ \diagup \quad \diagdown \\ CH_2 \\ \diagdown \quad \diagup \\ O \end{matrix} + H_2O$$

Cellulose Cellulose methylene ether

so that after the reaction there would be only one hydroxyl group remaining free. Present theories concerning the reactivity of cellulose fibers agree that the most effective manner of rendering cellulose more inert and less susceptible to most influences is that of suppressing the activity of the hydroxyl groups by chemical combination. An example of this is to be found in cellulose acetate in which two to three hydroxyl groups are combined with acetic acid; cellulose acetate fibers have little, if any, affinity for direct dyes, are more resistant to attack by mildew, have a lower moisture content than the original cellulose fibers from which they are made, and swell to a much smaller extent in aqueous liquors.

It may therefore be anticipated that by combining formaldehyde with cotton or viscose fibers it would be possible to influence their properties favorably as in the formation of cellulose acetate fibers, but formaldehyde is preferable to acetic acid in this treatment since the combination of cellulose with formaldehyde is very much more stable to caustic alkalis than is that with acetic acid (it is well known that acetate rayon is readily saponified when treated with dilute caustic soda). The formaldehyde compounds of cellulose are characterized by excellent stability to boiling detergent liquors such as are used in washing, laundering, etc.

In the first place it will be useful to consider some investigations of M. Schenk (Helv. Chim. Acta, 1932, *15*, 1088) which deal with the reaction of viscose rayon with formaldehyde in the presence of acetic acid and acetic anhydride which act as dehydrating gaents. Actually instead of formaldehyde itself, Schenk uses a condensation product of formaldehyde and propyl- or *iso*- propyl alcohol (di-*iso*propylformal) which easily splits into its components during the reaction and simultaneously combines with the water formed. As a result of the treatment the viscose is partly converted into a product containing combined acetic acid and formaldehyde and it is this substance which appears to have useful properties. Probably it is true to consider that the viscose, after the treatment, contains a proportion of an acetylated cellulose methylene ether, for the acetic acid can be easily removed by treating the rayon with caustic soda thereby leaving the cellulose methylene ether itself. The following is an example of the method of formation of such a product:

Three grams of viscose yarn are placed with 100 grams of acetic acid, 30 grams of acetic anhydride, and 25 grams of dipropylformal and the mixture maintained at 100° C. for a few hours. The product is then poured into water and the yarn thoroughly washed free from acid and by-products of the reaction. In this manner is obtained yarn which contains combined acetic acid and formaldehyde and which swells when immersed in caustic soda solutions as shown below:

Duration of reaction	*% Swelling in caustic soda of:* 0.0 *N.*	0.5 *N.*	1.0 *N.*	2.5 *N.*	5.0 *N.*	10.0 *N.*	*% Content of:* Acetic acid	For-maldehyde
0. hours	30	41	55	—	95	62	—	—
2	19	20	24	32	33	20	1.9	0.7
24	2	3	5	5	4	4	4.26	5.88
48	0	1	2	3	2	2	4.98	6.97
120	0	0	<3	<3	0	0	5.60	7.30

The extent to which the combined acetic acid and formaldehyde suppresses the swelling of the rayon in caustic alkalis as shown above and also by the curves in Fig. 1 is remarkable, and practically all this suppression must be attributed to the combined formaldehyde since it is not until cellulose has been acetylated to the extent of 34% that it fails to swell considerably under similar conditions. Also, during the swelling in the alkali the acetic acid is rapidly removed by saponification. Schenk also notes that the treated rayon has lost its solubility in cuprammonium solution and cannot be converted into viscose by the usual treatment with alkali and carbon bisulfide.

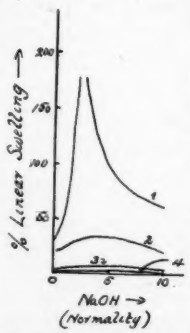


Fig. 1—The swelling of yarn after a formalizing reaction lasting:
Curve 1— 0 hours
Curve 2— 2 hours
Curve 3—24 hours
Curve 4—48 hours

In the reaction described above, the formaldehyde inhibits acetylation to a considerable extent and in this manner it behaves as when present in a parchmentizing liquor consisting of concentrated sulfuric acid. This inhibition of acetylation can be seen by the curves in Fig. 2 which indicates the degree of combination of viscose rayon under similar conditions with acetic acid with and without the presence of formaldehyde (dipropylformal).

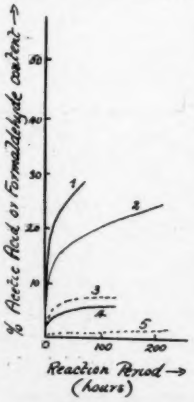


Fig. 2
- - - denotes formaldehyde content of heated viscose yarn.
—denotes acetic acid content of heated viscose yarn.
Curve 1 represents a reaction mixture containing 100 grams of acetic acid and 30 grams of acetic anhydride.
Curves 2 and 3 same but with 10 grams of dipropylformal added.
Curves 4 and 5 same but with 25 grams of dipropylformal added.

Schenk also prepared the formaldehyde compound (methylene ether) of viscose rayon and determined its resistance to swelling in caustic soda. The preparation was effected by treating 3 grams of viscose rayon with 100 cc. of acetic acid, 30 cc. of acetic anhydride, and 37.5 cc. of dipropylformal for six hours at 100 C. then washing the yarn thoroughly with water, and saponifying off the acetic acid by immersion for 72 hours in caustic soda. In this manner was obtained yarn containing 7.52% of combined formaldehyde and having the following swelling properties:

Normality of caustic soda swelling liquor	*Strength of treated rayon in grams per denier*	*% Strength increase*	*% Extensibility*
Untreated yarn	1.40	—	18.6
0	1.43	—	4.0
1	1.73	24	10.2
2	1.60	14	9.8
2.5	1.67	19	10.0
5	1.60	14	10.6
7.5	1.78	27	11.4
10	1.67	19	8.4

It is evident that in its combination of viscose rayon with formaldehyde under the conditions employed by Schenk considerable strength changes are produced, but these are irregular. Probably this is due to irregularities in the manner of combination since formaldehyde so very reactive that slight differences in the conditions of the reaction will have a large influence on the course of the reaction. This indeed appears to be the case from the investigations of F. C. Wood on the direct formalizing of cotton and viscose rayon (J. Soc. Chem. Ind., 1931, *50*, 411 T), and to which attention will now be drawn.

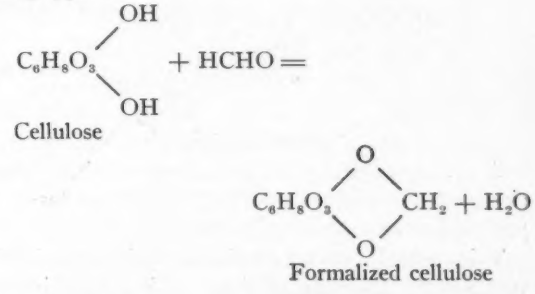
Firstly it may be pointed out that the combination between cellulose and formaldehyde may be assisted by the presence of either an acid or an alkali but especially the former. In either case, elimination of water formed during the process must be facilitated and as will be shown later the extent of this elimination largely governs the character of the product. Failure to recognize this fact has in the past led to much confusion concerning the properties of formalized cellulose fibers. On the one hand, it has been stated that the formalized fibers have greater affinity for dyes and moisture, while on the other a number of workers have reported that the treated fibers are more inert. In this connection a perusal of the patent of Eschalier (French P., 374724) and the work of Bruckhaus (Kunstseide, 1926, *8*, 115) will be found interesting since these publications express the two conflicting views.

Generally speaking it has in the past been a desire to improve the wet strength of viscose rayon that has prompted most research on the combination formaldehyde with cellulose. When viscose rayon is immersed in water it temporarily loses about one-half of its strength and becomes more extensible; this is considered a disadvantage and is believed to be due to the fact that moisture causes a swelling of the rayon to a much greater extent than is shown by cotton which does not lose its strength on wetting. Hence it was felt that this loss of strength could be prevented by treating the rayon such that it resisted swelling when placed in water, and formaldehyde with its well known condensing properties suggested itself as being particularly suitable for the purpose. Several of the early experiments along these lines have been described by Beltzer ("Les Matieres Cellulosiques," pp. 193-207).

At first it might be considered that if combination with formaldehyde could result in two types of viscose rayon, the one having a greater and the other a less affinity for direct dyes, then the method of combination of the formaldehyde within the cellulose molecule of these products would differ. Theoretical considerations along these lines have therefore led to the suggestion that formation of one type occurs thus:

(1) $\underset{\text{Cellulose}}{C_6H_9O_4.OH} + HCHO = \underset{\text{formalized cellulose}}{C_6H_9O_4.O.CH_2OH}$

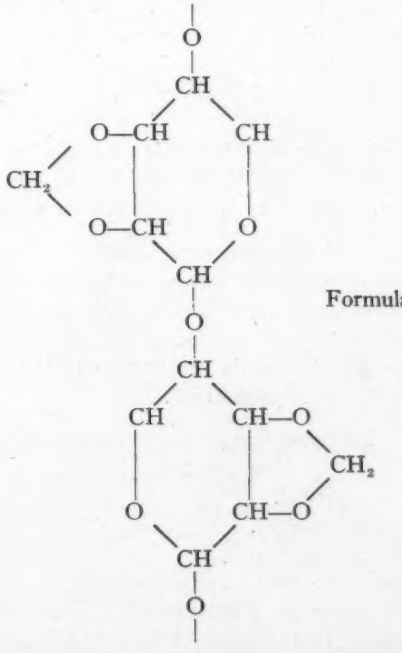
while the other type is produced by a reaction of the following type:

(2) 

Cellulose

Formalized cellulose

As a result however of experiments in which the various formalized viscose rayon products have been exhaustively methylated and the amounts of combined methoxyl determined, Wood (*supra*) concludes that there is no difference as regards the method of combination with formaldehyde and that all the products contain the true methylene ether of cellulose formed by the second reaction and having the following structural formula:



Formula A.

Since the properties of formalized cellulose fibers will be dependent on the amount of combined formaldehyde and also on the amount of moisture present during the

(Continued on page 399)

Rayon Dyeing and Finishing—8

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Consulting Textile Chemist

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CHAPTER V—DYEING AND FINISHING OF CIRCULAR KNIT RAYON FABRIC

(Continued from page 370, June 5 issue)

Peroxide Bleach

A few dyers prefer the peroxide method for bleaching circular knit fabric because they believe it produces a more pure and more permanent bleach.

This method, as used on circular knit rayon fabrics, is very simple, cheap and efficient. It is applied in the following manner:

1. Scour as usual.
2. Add sodium peroxide powder *slowly* to the front of the machine—two pounds peroxide per one hundred pounds fabric.
3. Run goods ten minutes.
4. Drop bath and proceed with dyeing operation.

The use of sodium peroxide in the above described manner cannot be recommended. Peroxide has a decidedly injurious action on rayon at and above 160° F.

The proper use of peroxide in conjunction with rayon is thoroughly discussed in Chapter VII, Dyeing and Finishing of Tricot and Milanese. The method of bleaching with peroxide described therein is obviously too expensive and bothersome to be applied to circular knit fabric in competition with the various hypo-chlorite methods.

Permanganate Bleach

Properly applied potassium permanganate will produce a very attractive bleach at a very low cost. Nevertheless its action is so "sharp" and the danger of tendering fabric is so great that its use in conjunction with rayon is decidedly not to be recommended.

Permanganate Bleach Procedure Per 100 Pounds

1. Scour as usual.
2. Rinse thoroughly.
3. Make up fresh bath.
4. Add one-quarter pound sulfuric acid.
5. Add potassium permanganate solution slowly. A pound of permanganate is dissolved in water. The concentrated solution is diluted, a little at a time, in a pail and liquor is slowly added from the pail to the front of the machine with a dipper.

   The permanganate is added so slowly that the bleach bath at all times appears either water white or, at the most, a barely discernible pink.

   The permanganate should be added so slowly that the last bit is not added until at least an hour, and preferably an hour and a quarter, is consumed by the operation.

   During the course of the bleaching operation the fabric will be gradually colored brown due to the deposition of manganese dioxide on the fiber.
6. Drop bath.
7. To a fresh bath add 2 lbs. sodium-bi-sulfite.
8. Run until fabric is white. About fifteen minutes is usually required for this operation.
9. Drop bath, rinse thoroughly, and remove from bath.

DISCUSSION OF DYEING PROBLEMS

The usual dyeing problems such as kettle streaks, penetration, fastness properties of finished fabric, etc., are too well known and understood to need further discussion here. In this book will be considered only the specialized problems due to rayon itself.

Barre Goods

The causes of barre fabric can usually be traced back to a difference in the physical properties of various skeins of the particular rayon involved—a factor entirely beyond the control of the man directly responsible for dyeing the fabric.

A second cause of barre fabric is variable tension applied to yarn during the winding or knitting operations.

Too often dyers adopt the attitude that, as they cannot reknit the fabric in the dyehouse, nor remake the rayon, they cannot in any way be held responsible for barre effects.

Whereas the dyer is not basically responsible for the cause of barre trouble, he is responsible for such excessive barre effects as might have been eliminated in the dye house by proper supervision.

The greatest single cause of barre effects is the reluctance of all dyers to use sufficient steam to raise the dye liquor to a strong boil. Many fabrics which are so unevenly dyed as to be practically unsalable when dyed at 130 or 140° F., can be made one hundred per cent

commercial when dyed at a boil. To insure the best results, circular knitted rayon fabric should always be dyed at a boiling temperature.

The use of relatively large quantities of salt during the dyeing process enables dyers to use less dyestuff than would otherwise be the case, and also aids materially in the production of uniform shades from batch to batch.

It is unfortunate that the use of salt greatly increases the barre troubles in circular knit rayon fabric.

A dyer primarily interested in the production of high class results will use salt very sparingly if at all, and will always use Glauber's Salt (sodium sulfate) rather than common. Obviously, the use of large quantities of salt is essential in the production of heavy shades. Fortunately less than one per cent of all circular knitted fabrics are required in dark shades.

The production or elimination of barre fabric is partly controllable by choice of dyestuffs. Some dyestuffs will produce quite level dyeings on fabric that would otherwise present so serious a barre effect as to be difficultly salable, The bulk of these colors, unfortunately, are not particularly fast to light or washing. The circular knit industry as a whole pays very little attention to the fastness properties of dyed fabric and is interested primarily only in the appearance of the fabric as sold across the counter.

Mills endeavoring to produce the best possible grade of merchandise from every viewpoint, and which use comparatively fast dyestuffs for underwear fabric are, in some shades, obliged to use dyestuffs of known uneven dyeing properties insofar as the barre effect is concerned. However, even in the case of comparatively fast dyes there is a very considerable difference in the dyeing properties of the various dyestuffs available. Even in the fast dye work choice of the best dyestuffs available for the production of each shade required aids materially in reducing barre.

Competition has so speeded up the dyeing process that at present most dyers are attempting to produce level satisfactory matches in a period of thirty to forty-five minutes total dyeing time. Whereas it is possible for a skillful dyer to produce dyeings on circular knitted fabric free from kettle streaks and matched to the desired shade, it is impossible to produce the best possible dyeing with respect to barre effect in so short a time. In order to eliminate or to cover as well as possible the tendency of any given circular knitted fabric to produce barre effect it is necessary for the dyer to allow the goods to run thirty minutes to one hour at the highest temperature obtainable in the dye kettle.

Consideration of the preceding pages makes it evident that barre effects though not basically the fault of the dyer can be very considerably reduced, and in some cases eliminated, by careful attention to all factors in the dye house. Keen price competition has much to do with the unwillingness of dyers to give the careful attention to the dyeing of circular knitted rayon fabric that is given to most other types of dyeing.

Dyeing Procedure

The problem of adding color to the dye bath is very simple when the shallow type of dye kettle is used. It is only necessary to choose reasonably level dyeing colors and add the same to the kettle with a reasonable degree of care to avoid splashing the color directly upon the fabric.

When the older deep style of kettle must be used the addition of dyestuff becomes very much of a problem. Color should not be added to the old style machine during a lesser period of time than ten minutes. The dyestuffs must be dissolved in a large quantity of water and must be added slowly to the front of the kettle by an operator who pours a small stream of dyestuff from one side of the dye box to the other by means of a small dipper or ladle; continuing the operation until all dye is added.

As is the case with the scouring process, details of dyeing procedure vary so considerably from mill to mill that it is impossible to give a dyeing procedure that can be considered representative of the manner in which circular knit rayon fabric is dyed. The following two procedures are not presented as typical nor as procedures that will give satisfaction under an unknown set of conditions. They are dyeing procedures that have given very satisfactory results in representative mills.

Dyeing Procedure—Circular Knitted Rayon Fabric—Soft Water Available—Scoured Fabric
Per 100 Pounds

(1) One pound of soap is added to the bath, the temperature of which is approximately 110° F.
(2) The necessary dyestuff is added.
(3) The fabric is allowed to run at 100° F. for five minutes.
(4) The steam valve is slightly "cracked" and the goods allowed to run for five minutes.
(5) The steam valve is opened wide and the bath is carried to the boil as quickly as possible (approximately one-half hour is required).
(6) The goods are run at the boil for twenty minutes after which a sample is taken.
(7) Necessary additions of dyestuff are made until the shade is matched. (In the production of self shades the matches are usually made in the wet state by the kettle operator.)
(8) Four-fifths of the liquor is dropped and cool water is added in sufficient quantity to allow the fabric to run in the kettle without "sticking" or chafing.
(9) Two to three per cent of finishing material (a softening compound) is added.
(10) The goods are allowed to run five to ten minutes.
(11) The goods are removed from the machine, extracted and dried.

Dyeing Procedure—Circular Knitted Rayon Fabric—Soft Water Available—Greige Goods
Per 100 Pounds of Fabric

(1) Fill machine with water.
(2) Load with fabric.

(3) Add scouring ingredients as per scouring procedure (see preceding pages).
(4) Scour for three-quarters of an hour.
(5) Add dyestuff slowly to the hot scouring bath.
(6) Continue scouring and dyeing operation until shade is attained.
(7) Drop bath.
(8) Fill machine with warm water—pour softening mixture into the incoming water. (Use two to three per cent softening ingredients.)
(9) Run ten minutes.
(10) Remove, extract and dry.

Fast Dyed Circular Knitted Rayon Fabric

Although dyestuffs possessing moderate to poor fastness properties can be used in the production of light shades on circular fabric, it is essential that dark shades be dyed with colors that are very fast to washing. For this purpose the developed colors are largely used.

The danger of chafing during the many steps of the diazotizing and developing process is so serious that most dyers have found it necessary to dye developed shades with goods turned wrong side out in order that such chafe marks as are formed will be inside the fabric and will not be noticeable on the outside of the finished garment.

Extra attention is paid to kettle loading, height of liquor in the kettle, etc., throughout the entire process in order that chafing may be reduced to a minimum. It has also become customary to use the best machine (most free running) for this purpose and to reduce the time of the diazotizing and developing bath as much as is compatible with the production of uniformly dyed fast colors.

Other than the special precautions to eliminate chafe marks, the application of diazotized and developed colors in circular knit rayon fabric varies in no way from the production of diazotized and developed shades on other types of textiles.

It is possible to dye circular knitted rayon fabric on the reel type of dyeing machine with vat colors when proper precautions are taken. These precautions consist in the use of sufficient hydro to maintain a reducing bath at all times; the use of caustic in such an amount that the bath is kept only slightly alkaline throughout the dyeing operation; choice of the proper vat colors; and the use of soap (with or without sodium perborate) as the oxidizing medium.

Dyeing Procedure—Application of Vat Dyestuffs to Circular Knitted Rayon Fabric
Per 100 Pounds of Fabric

(1) Scour as usual.
(2) Drop bath.
(3) Add 10 lbs. waste sulfite liquor retarding agent or glue.
(4) Raise bath to boil.
(5) Shut off steam.
(6) Add two and one-half pounds caustic soda.
(7) Add immediately, slowly, sufficient sodium hydrosulfite to render bath acid.
(8) Add one-half pound caustic soda.
(9) Feed in previously vatted dyestuff during five minutes.
(10) Run goods one-half hour.
Note condition of bath at all times. The bath must be maintained in a reduced mildly alkaline state, which condition can be easily checked by means of suitable sensitized testing papers.
(11) Sample.
(12) If addition of color is necessary, raise bath to boil, shut off steam, test for state of reduction and alkalinity; add necessary dyestuff, and proceed as in (10).
(13) When shade is attained, drop four-fifths of liquor.
(14) Run in fresh cold water, adding five pounds dissolved soap to the water as it flows into the machine.
(15) Raise goods immediately to boil.
(16) Boil five minutes.
(17) Drop bath.
(18) Give softening treatment.
(19) Remove and extract as usual.

DISCUSSION OF DRYING PROBLEM

Particularly because a soft, full hand is always to be desired on circular knitted rayon fabric, the methods of drying should receive more careful attention. It is to be regretted that much of the circular knitted fabric that is at present processed, is dried at temperatures sometimes exceeding 180° F. Such a temperature harshens the fabric and often removes so much water from the same that it is impossible for it to regain its normal moisture content during the finishing operation.

Realization of the difficulty of imparting the proper moisture content to over dried circular knit fabric by means of two quick passes over the existing finishing machines, has caused the more up-to-date dyeing plants to install humidifying equipment in conjunction with the drying system. Some plants have gone a bit further in this direction and have also reduced the temperature of their dryers. Both improvements lead to the production of soft, pleasing fabric.

In this respect it is interesting to note that the firms having drying rooms so constructed that the fabric is practically air dried, produce the softest circular knitted fabric on the market.

The discussion of dryers found earlier in this chapter eliminates the necessity of a more extensive discussion of drying at this point.

DISCUSSION OF FINISHING

The objects of the finishing operation applied to circular knitted rayon fabrics are:

(1) Elimination of wrinkles.
(2) Production of a smooth, uniform fabric.
(3) Production of uniform width.
(4) Addition of sufficient moisture to give fabric its proper regain.

(Continued on page 401)

PROCEEDINGS OF THE

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JUNE 19, 1933

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NORTH CAROLINA STUDENT SECTION

DR. R. E. ROSE was the guest of the Student Section of the American Association of Textile Chemists and Colorists of N. C. State College, May 16, 1933.

He gave a very interesting address at the meeting of the Piedmont Section, which was held in Greensboro, Saturday, and came to Raleigh to visit and inspect the Student Section of this college.

Dr. Rose gave interesting and valuable information concerning the manufacture of dyestuffs and kindred products. He stressed the fact that, although dyestuffs were produced in abundance and were important production factors of his organization, it has become necessary to develop other organic products from the intermediates used in the dyes. Interesting developments, such as the newer type of films, synthetic rubber, paints, etc., were discussed.

Respectfully submitted,

DAVID B. HARDIN,
Secretary.

APRIL MEETING, NEW YORK SECTION

THE meeting of the New York Section of the American Association of Textile Chemists and Colorists convened Friday evening, April 28, 1933, at eight-fifteen o'clock, at the Chemists' Club, 52 East 41st Street, New York City, Henry F. Herrmann, Chairman of the Section, presiding.

. . . Following the routine business of the Section, Mr. Augustus Kirby made a plea for assistance on behalf of the Salvation Army. . . .

Chairman Herrmann: Is there anything else to come before the Section before we close our business meeting? If not, we will proceed with the technical part of our program.

We have with us tonight Professor Allen Rogers, Director of Chemistry of the Pratt Institute. Some of us recall a number of visits that Professor Rogers has made to this Section. They have always been of the greatest interest. What he has had to say has been instructive. It gives me the greatest pleasure and I feel proud to introduce him this evening. He is going to address us on, "Odd Things in Leather."

Professor Rogers! (Applause.)

Proceedings of the American Association of Textile Chemists and Colorists

Odd Things in Leather*

By **ALLEN ROGERS**
Director of Chemistry, Pratt Institute

MR. CHAIRMAN, I thank you very much for inviting me over here to talk before this Section again. It is always gratifying for one who has talked before an organization once to be invited to come again.

In talking to this Association, I hardly know what to say. You might be interested in the application of dyestuffs to leather, or you might not. So what I thought I would do would be to talk in a rambling way about some of the things with which we are not so familiar, in the applications of leather. I have brought my bag with me and I shall have to fish out some stuff here. I haven't opened this bag since I was up to the New York University and talked to the boys there. I was also up to C. C. N. Y. and talked to them on the same subject. So I have my speech all prepared.

The leather industry, as I think you all know, is the oldest of the industries. In fact, it started in the Garden of Eden. I think I mentioned before when I talked to you about it first that in Genesis, the Fourth Chapter, the twenty-third verse, you will find that the Lord God made coats of skins, and clothed them. This was brought about from the fact that Eve wasn't quite satisfied with all the good things she had in the Garden. She wanted that apple and so she tried to get Adam to help her get the apple. He said, "I don't care about apples," but being a good, dutiful husband, he finally consented and she started to climb the tree, and he boosted her up.

She said, "I don't care" and tossed the apple to Adam, and then they decided things were different than they appeared to be. But the only trouble was that every time Adam hunted around for his dress-suit he would find that Eve had used it for salad. That is why they called on the Lord God to make the coats and skins and clothe them.

Just what process was used in the Garden of Eden, history doesn't tell us. No doubt, they didn't bother to remove the hair from the pelt of the animal. But they soon discovered that if animals' skins were not treated in some way they would putrify and decay, especially when a rainstorm came up. They no doubt discovered some means of preserving the pelts.

Possibly the earliest method of preserving pelts was by means of smoke. They still use the smoke cure today, and in history we read—in the Bible, Nick Carter, or something like that—that, "I am like the bolts in the smoke."

That means it is all puckered and smoked up.

The raw hide of course could not be used as such because it would become too stiff and it could not serve as a protective coating to the body.

Outside of the smoke cure, probably the oil tanning method was one of the earliest employed and in the Iliad you can read how the serfs dispersed about, stretched the moisture out, and drank the unction in. That refers of course to the production of leather by means of oil tannage, in which the oil or grease of the animal, in connection with the brains of the animal, were smeared on the flesh side and allowed to be taken up. We have today a process which is similar to that described in the Iliad. This process is used in the production of chamois leather. Chamois skins are oil tanned products.

This (sample) happens to be a chamois skin. Chamois skin is perhaps the most common example of an oil tanned leather that we have. We have other oil tanned products, such as moccasin leather, and things like that, but the chamois is the thing with which we are all familiar. We also apply the oil tanning process to the manufacture of certain kinds of furs.

Chamois originally was made from a goat, the chamois goat. The reason that the chamois was used is probably because the chamois is an animal that lives in the Alps. He jumps from rock to rock and slides down over the rocks and bangs himself up, and the skin is no good for leather, because it has a poor grain. However, some early tanners found they could treat it with oil and make a fairly soft material for washing windows. They didn't wash automobiles then, but they used it for various other purposes. Then the supply of chamois became more or less exhausted—the animal is almost extinct now—and some Yankee (or some other fellow) found that if he took a sheepskin and split it in two, and took off the grain, he had a rough leather underneath, which is called the flesher, and by treating that flesher with oil, he got a soft leather which could be used, as we know that chamois leather is used, and that is what we know today

* Presented at April 28th Meeting, N. Y. Section.

as chamois. It is called chamois skin. It is not chamois skin at all but it is a sheepskin flesher.

The method used is to treat the skin with cod-oil. It is banged into the pelt, and then put in the cellar and allowed to get hot. It is taken up just before it burns up. Then it is treated with some more oil, hung to dry, and finally washed. The oil that is pressed out is called moellon, which is used for various purposes in the leather trade. Then the skins are treated with soda and washed out, the wash water is treated with an acid, and we get sod oil. We then have, as a result of this treatment, a leather with which we are all familiar—chamois.

There have been some recent developments in the manufacture of chamois leather which I won't take time to go into which make it very much easier to manufacture the leather, and also there is one development which makes it possible to stand higher temperatures than was possible the old style chamois.

I simply mention chamois as a type of oil tanning which no doubt Adam and Eve, or maybe Cain and Abel, developed in the Garden of Eden.

The next process of tanning probably was the alum tanning method of producing an imputrescible material from hides and skins of animals. When I speak of hides and skins I must remind you that the two terms cannot be used indiscriminately. When we refer to a hide we mean the covering of a large animal and when we speak of a skin we refer to the covering of a small animal. Just where a skin becomes a hide it is hard to say although of course some animals never have hides and some animals may have had skins at some time or other.

The third method of tanning was alum tanning and no doubt that was more or less an accidental discovery. Probably the pelt was thrown down into some brook where there was alum and when they pulled it out they found it didn't putrify, but that it became white and could be worked up and made into a very good product.

So alum tanning is used today, perhaps the same as our ancestors used it a thousand years ago. The development of the chemical industry has made it possible to have other salts of alum such as sulfate of aluminum, and we have found that the basic salts are better than the straight neutral salts. But it is still alum tanning, and that has been used for thousands of years. Sometimes we think that the leather industry is sort of antiquated, but these antiquated methods are really right up-to-date.

The first leather no doubt was used for protection of the body and also for making tents. At some time or other they probably had more hides or skins than they knew what to do with so they threw them out in the backyard and they found that the hair came off. So some man who would have been known as a research chemist in these days investigated the thing and he found that it was on account of the rotting that the hair came off. So they rotted all the hides after that, to get the hair off, because they liked them better with the hair off than they did with the hair on. That process is still used in what we know as staling for sheepskins or sweating for hides. In the manufacture of certain types of sole leather, the hides are allowed to get rotten or putrid and the hair falls out, and it makes a very firm leather.

Later on, when they began to build houses and they discovered that lime could be used to stick bricks together, probably a hide at some time or other was thrown out into a puddle of lime, and they discovered that it also took the hair off. That was a wonderful discovery.

So the early inhabitants of this earth removed the hair by means of lime. But when they had the hair removed by lime they found they couldn't make a satisfactory piece of leather out of it, so they gave it up, and the caveman's wife who used to do the tanning threw it out the kitchen door. The chickens came around and somehow it got out to the hen yard, and the droppings from the chickens got on the hide and they found it became all soft again. So that process was used for converting that hard rubbery product into a flexible material up until twenty-five years ago, and the process was known as bating or puering.

After a hide has been treated with lime or sulfide, which we have recently found could be used, we have to remove the chemical, and the thing that was used for thousands of years was chicken manure, or in the case of goatskins, dog manure.

About twenty-five or thirty years ago—time flies by; I am an old man, and of course thirty or forty years don't make much difference in my young life—it was found that the action of these manures was due to an enzyme and that enzyme was found to be pancreatin, and also in the natural product there is ammonium chloride. A product was developed which was called "Oropon." Other manufacturers are now producing similar products called "Puerin," "Derma Bate," and so on. They are all dried pancreas, mixed with ammonium chloride. This removes the lime and sulfide and brings the skin back to a flexible condition.

Although we have been familiar with leather for thousands and thousands of years, perhaps millions, it has only been in the last twenty-five years that we have gotten away from some of these antiquated methods.

The next method of making leather was a vegetable tan process. That was discovered probably in connection with the alum process. They knew that certain herbs, certain roots or barks, produced color on leather, and incidentally they found that certain of these barks helped to preserve the leather, to make a better product. We don't know just when it happened but it was probably thousands of years ago; we know it was thousands be-

cause we know that in Tut-ankh-Amen's tomb there was some good leather found that was made by the vegetable tan process. That process has been handed down. We are still using vegetable tanning materials in the manufacture of sole leather. In fact, ninety-five per cent of our sole leather is vegetable tanned, and the most common vegetable tannage that people used to use was oak, but there is no oak tanning any more. Hemlock was used a great deal, but there is not very much hemlock used now. Chestnut was used a great deal but there is not very much chestnut any more. We do, of course, have chestnut in some of the Western forests and in Virginia and certain other places, but most of the tanning material today comes from South America in the form of quebracho extract. That is mixed with a certain amount of hemlock that is available, and a with a certain amount of chestnut, mangrove and other vegetable tanning materials.

The advantage of the vegetable tanning material for sole leather is that it gives body, it gives good cutting qualities, it channels well, it feels good on the foot. Some of the modern methods of chrome tanning give a leather that wears better, but it is not so comfortable.

Synthetic Tanning

Then we have, of course, synthetic tanning materials that are used in connection with vegetable tanning materials, which hasten the time required for the process. Fifty years ago it took about eighteen months to tan a piece of sole leather. Today sole leather is tanned in about thirty days.

Some people think that it doesn't wear the way it used to but I remember, even in my young life, that when I was a youngster I would get a new pair of shoes and walk up the aisle in Sabbath school and those shoes would squeak all the way up the line. The leather was very hard. It didn't wear out. The tops of the shoes used to wear out and they would patch them, but they don't patch shoes any more. They wear out the soles first. The soles of our shoes are flexible, and we wouldn't wear that old hard leather that was worn by our grandfathers. We want nice, soft, flexible leather such as we get now in the modern sole leather and in the modern shoe.

The process of vegetable tanning was followed by chrome tanning, and the chrome tanning process was the one that put the tanning industry on a scientific basis. The production of chrome tanned leather was accomplished by an American wool dyer. Schultz was not a tanner but he was a chemist employed in a color house up in Boston. He was selling dyes to Robert Fouderer in Philadelphia, and Robert Fouderer was producing a morocco leather used for bookbinding, pocketbooks, and so on. They couldn't sell very many morocco skins, but there were a great many of those skins available.

So in talking with Schultz, Fouderer suggested, like all tanners and other manufacturers suggest today, "Well, if you could only do this with that or that with this you would make a fortune."

That is what Fouderer probably told Schultz, and Schultz believed it.

So he set to work upon a method of producing some leather by means of chrome, thinking he would perhaps use the same method used in wool, in which he chromatized and then afterwards added logwood or something else to dye the wool, and he found that by using dichromate of potash and hydrochloric acid he could saturate the pelt, reduce it with hypo, and get a chrome that was fixed.

That was not new to Schultz, that chrome could be fixed by the hypo, because that had been discovered a great many years before that, but it was not considered to be suitable for leather. The basic sulfate of chrome was used, and it was green in color. The tanner said, "That isn't leather. That is green. Leather ought to be brown."

Schultz carried on some experiments and showed them to Fouderer. They looked pretty good but after they got it tanned they didn't know what to do with it because it didn't act as a vegetable tan. The darn stuff got stiff as a board. But he wasn't discouraged. He washed the stuff and when he washed it with soap he found that it became nice and flexible, and he also found he could color it the same as you color wool.

So he took out some patents. The Schultz process is a two-bath process of tanning. He sold them to Fouderer for three thousand dollars. Robert Fouderer then developed the Vici kid which made the Fouderer family multi-millionaires. The A. C. Lawrence Company infringed the patents. They made Vici kid or the equivalent and they became very wealthy and Schultz still had the three thousand. Then there was a lot of litigation between Fouderer and A. C. Lawrence and after seventeen or eighteen years, when the patents had expired or pretty nearly expired, there was a decision against A. C. Lawrence and so Fouderer got some more money.

That was the process and still is the process that is used by the goatskin manufacturer today in making what we call Vici kid. "Vici kid" is a trade name that belongs to Robert Fouderer but everybody uses it, because we are accustomed to talking about a certain kind of leather as Vici kid just the same as we talk about a sparkling wine that has a fizz to it as champagne, even though it was never near champagne. It is the same with the goat skin.

Later a man over in Newark named Martin Dennis, after a lot of experimentation, produced a practical one-bath chrome process for tanning which could be used on sheepskin, calfskin, side leather. After many trials and tribulations he finally produced a satisfactory product and most everybody today is using the one-bath process. They

are using the material which is manufactured by Martin Dennis and which is known as Tanolin. There is Corion and there is Tanolin and all other kinds of names, that is trade names. I am not advertising Tanolin but that happens to be like champagne, something that people know about. A lot of tanners make their own one-bath chrome liquor.

So we have now for the uppers of shoes, chrome tanned leather, and vegetable tanned leather for the soles of the shoe. We are walking on the soles of our ancestors but we have on the uppers only the upper leather of our fathers.

Instead of going to the cobbler to have our shoes patched, we don't have them patched any more because chrome tanned leather doesn't wear out. Chrome tanned leather has an advantage over vegetable tanned leather for the upper part of a shoe in that it holds its shape.

Of course, you are all young fellows around here. I am an old fellow and I can remember seeing shoes with every corn and bunion sticking out. You don't see shoes like that any more. People don't have corns and bunions. If they do, you don't see them because chrome leather doesn't conform to them. And probably people don't grow them as much as they used to. It makes a very much nicer looking piece of leather.

Chrome leather, the upper leather of shoes, is made in all kinds of designs and colors, and the tanners wish the day would come when people would wear high shoes again. Especially they wish that the ladies would wear high shoes again, but the ladies make up for it in a way because instead of having just one pair of shoes now they have a dozen. A lady today must have a different pair of shoes for every dress that she possesses. The shoe must conform to the color of the dress.

Kinds of Leather

So we have, for instance, a goatskin here of this shade to match a certain dress, and if she has a dress with checks in it she can have leather, of course, made with checks in it. You can have all kinds of fancy designs on the leather to match the colors of the different dresses.

The skins that go into the upper leather of shoes, as I say, are goatskin and calf and side leather. Goatskins and kid mostly go into ladies' shoes. The calf and side leather go into men's shoes. Kangaroo goes into men's and ladies'.

This (sample) is a kangaroo which is finished with the same finish as Vici kid, and kangaroo is perhaps one of the best leathers because it wears very well. The grain does not scuff the way goatskin does. One great disadvantage of the goat is that it has a grain that scuffs up very easily, while the kangaroo does not.

A popular leather for men's shoes, if it wasn't for the price and the uneasiness which your feet feel when you have them on, is Cordovan. Cordovan is a wonderful shoe for wearing quality but is very hard on the feet.

This is a heavy side leather (sample) for men's shoes. It is made either of smooth or Scotch grain or box grain. They are all out of the same animal, and box calf usually comes from cowhide. They take leather that is poor and in the tanning it puckers up and gives a bad grain or break. Then they roll it on the machine and bring up little squares on it, and that is called box calf, and it is a nice piece of leather because it is a box calf.

These are goatskins, of course, chrome tanned with different kinds of finishes. (Samples.)

This happens to be a monkey skin. Not very many monkey skins are used in shoe leather. (Sample.)

A very popular leather is patent leather. It gets its name from "patent," because at some time or other a fellow took out a patent. But patent leather or enameled leather is only leather that has been painted. (Sample.)

The old style patent leather was made by the vegetable tan process and later by the chrome, and then degreased and when you degrease a skin you take out all the nourishment. Then you put on a coat of varnish, and then another coat of varnish, and another coat of varnish, and it looks very pretty, and then when you go out in the cold with those shoes on the leather all cracks to pieces.

That was the old style patent leather but the modern patent leather is made on a non-degreased skin. Sulfonated oils are usually used for the fat liquor. It doesn't require degreasing, and the varnish doesn't sink in, and it only requires one coat of varnish where it used to take four or five, and today you can get patent leather to which you can apply a knife and pull it as hard as you please without pulling the grain. This piece of patent leather is probably four or five years old, and it doesn't crack.

That demonstration is what the shoemaker tries because when he lasts the shoe, it has to stand that kind of treatment. He doesn't care whether it cracks after people buy the shoe or not, but if it stands that treatment, it will stand up in the shoe.

This is side leather. (Sample.)

Today of course a lot of patent leather is used. It has its ups and downs. Sometimes it is popular and at other times it is not.

Patent leather is made in all kinds of colors. The opalescent or bronzy effect is made while the varnish is still slightly moist by blowing subnitrate of bismuth on and then rubbing it off, and that is what gives it that finish. sometimes they use fuchsin, magenta or methyl violet to give that effect.

I have a lot of samples here. This, of course, is another goatskin.

These are various kinds of leather.

For ball shoes the women like silver leather, so silver is applied to the skin and rolled on; also gold leaf.

In the manufacture of shoes you have, of course, the sole, you have the upper, and you have also the welting which joins the bottom of the shoe to the upper part, and the best welting is made of pigskin. These are bacon strips. They are tanned and they are very strong, and serve as a good binder for the lower and upper part of the shoe.

Uses of Leather

We used to make a lot of automobile leather in this country but lately, with closed cars, we don't like leather so much, and especially because the ladies don't wear as heavy clothes as they used to. When they get into a car they object to the cold leather, so we have had to get upholstery of various kinds for automobiles. The tanners had to try to meet that competition and so recently tanners have been putting up leather to look like fabrics. This paisley shawl effect makes a very attractive piece of leather and when the lady gets into a car that is upholstered in this material she thinks it is a fabric, and so it is all right.

This particular piece of leather is out of the car that was used by the Prince of Wales when he was here a few years ago. They built a car especially for him and they put this kind of leather in it. This was made to look like antique leather, so the Prince wouldn't think the car was made especially for him but as though it was an old car that had been handed down for generations. That antique leather is made by curing and rolling the stuff all up and putting in some carbon black and turpentine and then rubbing it off. That makes it look old.

Then for automobiles they have patent leather effects that are printed the same as the shoe leather is printed.

Here are various designs of leather for automobile upholstery. Some of these have pretty flower designs.

Another type of leather is leather for gloves. Glove leather must be entirely different from shoe leather because it must have all the stretch that you can get. It mustn't be hard like the sole of a shoe. It mustn't hold its shape like the upper of a shoe but it must stretch because when you put it around the finger it has to conform.

Glove leather is made from small kids or lambs, and the process of tanning is different in that you have to lime much longer, to open up the fibres. You have to bake much longer, to open up the fibres still more. You must have a nice, silky grain. And in some cases the grain is removed. It is limed for forty or fifty days and the grain scraped off. That is called frizzing. When you buy a Mocca glove, or what we call undressed, the grain has been removed. These are colored with pigments very largely. Some are colored with acid or basic colors.

Coat leather today, what we call windbreaker leather (quite a bit of it is being used at the present time) is made from the fleshers the same as chamois skin. This is the regular standard coat leather.

This one is made from gamma acid. (Sample.) Sometime in the future many of our intermediates are going to find quite extensive application in the tanning of leather, but this is a little ahead of the times. I have some patents on the use of some of these intermediates but at the time they begin to use them my patents will all have expired, so you fellows can use them.

These are the ordinary materials with which you are all familiar. I thought perhaps I would show you a few things in which leather is used where we don't think of it being used so much. (Samples.)

This is a sheepskin. Sheepskin is about the only thing that can be used for this purpose.

This is a gun sling that was picked up on the fields of France. The French picked up a lot of them right after the war was over. We sold them to them. We haven't received our pay yet but we sold them, all right, with a lot of other material. There was a fellow who lived up in The Bronx who bought a million of these gun slings at a cent apiece. He took the brass off the sling and got two cents for that. He was a good New York businessman. Then he had the leather left. I worked up a little process for him whereby he could take this leather and clean it, dye it black and emboss it. He bought a buckle for two cents, put them together, and sold them for fifteen cents wholesale, and then the wholesalers sold them for fifty cents retail.

This is a nice belt because it has a history. Some of these belts have the fellows' initials carved on them. Whether they died on not I don't know but probably they did because they were picked up on the fields.

Within the past few years there has been quite a demand for reptile leather. This is a genuine snake. This is another snake leather. This is used for trimming and also some on the uppers of ladies' shoes but most snake is used for trimming. (Samples.)

Lizard has been quite in demand. This is a genuine lizard which, of course, is colored. (Samples.) They can color it any color they want. This is a lizard that is made out of a rabbit. Even if you are a good judge of lizard it is difficult to tell which is the lizard and which is the rabbit. Rabbits of course don't have that kind of shape. I had the full skin here but people kept on borrowing from it, and now I only have this left. But you know rabbits don't have legs like a lizard.

It is rather a conundrum how to get a rabbit to have legs that look like a lizard's, but it really isn't difficult. Chemists can do that easily. All you have to do is tan the rabbit skin in the shape of the lizard skin, which is about this big, and then you cut things that look like legs,

and take a hot iron and pass it over each one of those things, and they pucker up and look just like the natural legs of a lizard.

Shark Leather

I have been sort of interested in shark fishing, and in shark leather for quite a number of years. Sharks are wonderful animals when you get to know them personally. (Laughter.) They are very nice. They are quite kittenish at times. Only you have to be on the watch for them. Sharks are not man-eaters as a rule. There are only a few of them that really like to eat men. The rest of them will get out of the way of men. I have done a lot of fishing. I have some leather here that comes from sharks.

There are a good many kinds of sharks. This happens to be a tiger shark. (Samples.)

This shoe is made from what is called a nurse shark. Nurse shark and all shark leather has over its surface a layer called shagreen. It is a calcerous matter and before you can make leather you have to remove it. When they get the shagreen off, they are able to produce commercial leather out of it. But once you have a leather like this you can hit it, you can go out into the woods with it, bump over rocks, and you can't scrape off the grain. It is very fine for children's shoes and is also good for shoes for grownups.

I wore these shoes until I got tired of wearing them. This is nurse shark leather on the top and the sole of the shoe is a leather made to imitate imitation leather. We are so interested in having imitations we now have to make leather to look like imitation leather. And it wears very well.

This leather is from a so-called spike shark. The spike shark has what look like cat's teeth all over its body. It is all right to smooth them that way (indicating), but not this way, and if you are going to jump on a shark's back and hang on, be sure that it is not a spike shark because it will tear the seat off your trousers and maybe take off some flesh, but it makes a pretty leather when finished because it looks very much like the bark of a tree.

I think I have some bags that are made from spike shark. These are all samples of spike shark.

If you tan a shark leather with the shagreen on it will wear forever, from generation to generation, but the trouble is you can't sew it. The minute you sew the stitch, it is so sharp it cuts the stitches.

The first pair of shoes I had made for my youngster —he was about seven or eight years old then—were made with the shagreen on. He couldn't wear them out. Then I sent them down to Redfield who was Secretary of the Interior and he had them on display for quite awhile, and when my kid got his shoes back he was very proud to think they had been down to Washington in the Department of the Interior.

The demand for shark leather has become so great that now they imitate the shark leather. This is a genuine shark leather, this the imitation. (Samples.) This bag is an imitation shark leather designed from the piece of leather I showed you before, the tiger shark.

That is another shark leather.

Here are some bags. These little pocketbooks are made of shark leather.

In speaking of the various kinds of leather I showed you a sample of pigskin here. You notice the pigskin has on the flesh sides little pores. The dog has the same thing, so has the bear, and so has the human being.

This leather here is from a human being. It is a very fine piece of leather. The only trouble is we don't seem to get very much of it. This particular piece was taken from an Italian street cleaner down on 23rd Street and Second Avenue. He was run over by an automobile, and killed. His people didn't come around for him, so his skin was available. It makes a fairly good piece of leather. It looks like pigskin. It is very difficult to tell the difference.

I had some nice smoking-caps when I was going to school at Philadelphia, made from various parts of the human anatomy that the boys brought home from the dissecting rooms, but I lost them. This is the only thing I have ever been able to hang onto.

This is walrus. This isn't good for anything except buff-wheels.

Whale doesn't make a very good leather, because it is too thick. You can make very good leather out of whale's intestines. It is a sort of baggy leather. Whales' intestines I guess must be seven or eight hundred feet long. The longest I had was one hundred and fifty feet. I only had a little part of the intestines. It may have been its appendix, I don't know.

You can make leather out of the stomachs of sharks.

Rawhide, as I mentioned, can't be used for leather because it is too thick, but it is used for ukuleles, banjoes, lamp shades; it is used on saddles, and scabbards, and of course rawhide has a lot of different applications.

Other Sources of Leather

You don't always have to have the outside of an animal to make leather. This is called zephyr leather and it is made from the appendix of a beef animal. A beef animal has an appendix about four or five feet long, and when a cow has appendicitis she has "ap-pendi-set-us." But the membrane is taken off and is used for the caps of perfume bottles. They also use it for fancy lamp shades and a lot of different things. It can be made into sheets like this and it is sometimes called parchment, but it is made from the appendix.

There is another use for the appendix. It is put on the board and wrinkled up like that so that it looks almost

like an alum-tanned leather. That is used on the valves of a player-piano. It is also used for caps.

Another part of the animal that is used is the intestines of the sheep. This is used for producing surgical sutures. When you have sewn up a wound with catgut, it isn't catgut at all, but it is sheep's intestines.

These intestines are split over a knife into what we call a rough side and two smooth sides. They are cleaned and then spun together and a Number 2, which is the catgut that is used mostly, this size here, is made, five-ply, representing two complete intestines. The break on that is about twenty-three pounds. The catgut is absorbed in the system. When you have an interior operation they use catgut because that is absorbed. They don't have to go down in and take it out. For outside stitches you are sewed up with what is called dermal suture, and the dermal suture is made from the silkworm gut. That is, the silk worm is taken just before he starts to spin the cocoon, and put in boiling water. That kills him. He is then squeezed through an orifice. That hardens and it is called silkworm gut. It is colored black so that it can be seen after the stitch is applied. You can have it in colors, red, black, or something like that.

This is the same stuff that you have on the fishline leader. That is silkworm gut. There is a product that comes in from Japan called "Tagussah," which is a silk with some kind of a sheath on the outside. It is a gelatinous material hardened in formaldehyde. It is somewhat cheaper than silkworm gut and some surgeons prefer it.

So, the intestines of the sheep are used and one concern in Brooklyn with which I have been connected ever since they started, about 1912—they are the largest manufacturers in the world—produce about sixty per cent of the sutures used in this country. They utilize the intestines from five thousand sheep a day. They use what they call the small ends, which are twenty-eight feet long. So you see there are a lot of people being sewed up.

Other parts of the animal are used for surgical purposes. This is a sheep's bladder. That is used for certain surgical operations. The membrane of the sheep's intestines is also made into strips and little disks and for operations that are very bloody that thing is sometimes put on to absorb the blood. It is afterwards absorbed itself.

These suture materials are chromatized, in order to have them absorb more slowly. An ordinary gut, what is called a plain gut, will absorb in about eight days. When you chromatize it, it absorbs in ten, twenty, or forty days. It depends on the nature of the operation. If you have a great deal of pus, you want it to last longer, and so it is chromatized. So it is really a tanning proposition.

The only reason I mention suture material is because that is a branch of the tanning industry. This is a chromed gut. Gamma acid also makes a very good suture material.

These sutures are put in tubes and then sterilized at a high temperature under pressure. The storing fluid is xylene. So when the surgeon wants to use the suture he simply breaks it at the engraving mark, takes the suture out, and he is ready to sew you up.

There are a great many things being done in surgery that are interesting. Operations are now being done on the arteries. One of the surgeons here in New York performs very wonderful operations. He cuts the arteries leading to the heart and if he finds a clot in there he sutures off the arteries, cuts a hole in the artery, reaches in, pulls out the clot, sews the artery up and starts the heart up again. That operation has to be done within two minutes.

Another application of leather is in the production of instruments for operations for hernia. They very often open up, locate the hernia, cut into the patient's leg, sew off the hernia, and leave that strapped on, so that the live tissues can be in contact with the hernia. Then when the hernia is healed they cut the tissue and sew the fellow's leg up. Now we find that we can take that tendon out of a beef animal. It helps people with hernia and at the same time it helps the people who have to eat that beef because the meat tastes much better with that muscle out. So when you get a beef-steak with this muscle out you know you are getting a better beef-steak than you used to get.

So the leather business goes into various phases of life that we don't often think about. It goes into the intestines of animals and into fish, into the shark, which is not really a fish (it is a mammal), and into seals, and porpoises. A porpoise makes a wonderful suture.

This is another form of suture material which is used for tennis strings. The intestines of the animal are also used for tennis strings and ukulele strings. It is also used in machinery belting.

Another form of rawhide is this pelt pin made from the water buffalo. It is cut into strips and used to join together the clippers of clipper belts.

I have talked in a rambling way about some of the things that you don't ordinarily hear about that are connected with the manufacture of leather, and it hasn't been a very highly scientific paper, I assure you. (Applause.)

Discussion

Chairman Herrmann: We certainly appreciate your talk, Professor. Rather than a rambling talk I would call it a liberal education in leather.

I am almost afraid to ask for questions for fear that we may overrun our time. But if there are any let's have them.

Mr. Ephraim Freedman: Mr. Chairman, I would like to

ask a few questions if I may. This topic has been rather interesting to the members present.

In our experience with textiles, quite frequently we run across a problem which gives us much cause for concern, and that is the crocking or rubbing off of color. That is overcome in many instances. However, when it comes to leather goods that problem, in so far as it concerns leathers that are worn or made up into garments, has not yet been solved to any great degree, and that holds good apparently more with suedes than it does with grain finishes.

I was wondering just what progress is being made along that line, that is, along the line of removing the excess dyestuff so as to reduce the transfer of color, or the removal of color.

Dr. Rogers: About once a month someone comes in and wants to know, "Can you get some way to prevent crocking of this garment leather?"

The reason it is going to be practically impossible to do that is because that is a suede finish, and it is all full of little particles of dust, and if you put anything on to try to hold that color in then you overcome the suede effect. I don't think it will ever be produced, but in the case of grain leather that is not a problem. You can put a finish of shellac on the grain side, or a lot of those dull finishes, pigment finishes, and they don't smut or crock.

Of course, not very much attention is paid to the flesh side.

I think if anyone is able to discover a means of doing that he will make a lot of money—just like Mr. Schultz. They always say, "If you can get a nice suede leather that won't crock you will make a fortune."

Mr. Freedman: The furniture leather tanners apparently have solved that problem to a much greater degree than have those making garment leather.

Dr. Rogers: In furniture leather they use finishes. Pigment finish is a varnish and, of course, the varnish won't crock. But furniture leather is not a straight dyed leather. There is some finish on the top like flaxseed, if it is a water finish, or gum tragacanth, or casein, or egg yolk. They all harden and prevent crocking. Or they use some of these modern lacquers. Of course, they don't crock. But they don't make furniture out of the regular suede. If they did they would have a little trouble.

Mr. Freedman: May I ask a couple of more questions?

Chairman Herrmann: Surely.

Mr. Freedman: Is the split leather more durable than the grain leather?

Dr. Rogers: The first split is really, I think, better than the grain. The grain of a leather is made up of scales. It is like scales on a fish. You can take a magnifying glass and look at the back of your hands and you will see the scales on your hands. From underneath, the fibers are coming up through. Those scales are coming off all the time, so that the closer you cut to that grain the weaker is the leather. But if you take off the top grain and then take another deep cut for the first split, that is the strongest part. Then when you get the middle split, that is very weak. When you get to the flesh, that is strong.

Mr. Freedman: Many people are under the impression that because an article is made of leather that it is more resistant than a garment made of textile fibre and for that reason they are quite put out about it when leather scuffs. They forget that leather is apt to skin, and that it is likely to scuff just as readily, except shark skin and some others that show greater resistance.

Dr. Rogers: Yes, most of them do scuff.

Mr. William A. Kingman: Isn't it a fact that most all leathers today have a pigment finish on them?

Dr. Rogers: I wouldn't say that just now most all leathers do. There was a time when that was true with respect to practically every leather, especially following the War and during the War. We ran out of dyestuffs and they started using the pigment finish at that time. It was so good that they didn't want to come back to the colors again but four or five years ago there was a tendency to go back to the aniline dyes, and there is quite a lot of aniline leather back on the market. However, I would say that practically everybody who does any coloring of leather puts the coal-tar color on and then gives it a little bit of pigment on top. That covers up some of the defects. You can't cover up the defect with the dye but you can cover it with paint and, of course, the pigment finish is paint.

Mr. Kingman: Black leather is the only one that doesn't have pigment.

Dr. Rogers: No, you don't have to so much. You can cover up anything with pigment.

Mr. Edward J. Volkman, Jr.: In those pigskins what type of color is used now? Is that a pigment color?

Dr. Rogers: Yes. Those are pigment colors printed on like block printing, when the leather is damp.

CALENDAR OF COMING EVENTS

Outing, N. Y. Section, June 23, North Jersey Country Club, Paterson, N. J.

* * *

Outing, Piedmont Section, July 1, Mayview Manor Hotel, Blowing Rock, N. C.

* * *

Annual Convention, Chicago, Sept. 8 and 9.

EIGHTIETH MEETING, RESEARCH COMMITTEE

THE Eightieth Research Committee meeting was held at the Bureau of Standards, Washington, D. C., March 31, 1933.

The following were present:

L. A. Olney, Chairman; Wm. D. Appel, Howard D. Clayton, Roland E. Derby, Carl Z. Draves, Milton Harris, B. L. Hathorne, Henry F. Herrmann, Heyward F. Lawton, Hans Meyer, Wm. R. Moorhouse, Donald H. Powers, Robert E. Rose, Wm. C. Smith, A. Newton Graves.

The Chairman presented certain matters in connection with the Year Book and stated that its publication would be delayed somewhat owing to the fact that an endeavor was being made to bring all reports up-to-date and also produce a Year Book with greater uniformity of arrangement between the different sub-committee reports and reports of Local Sections.

Wm. C. Smith reported in regard to certain phases of light fastness upon which he was working at the present time.

Dr. Harris discussed the three projects, namely, Action of Acids with Wool; Action of Alkali with Wool, and Action of Dyes with Wool, upon which he is working under an allocation from the Textile Foundation.

Donald H. Powers, Chairman of the Committee on Research Program reported in regard to a meeting of that committee which had been held earlier in the day. In this connection the matter of Advisory Committees to assist Research Associates was discussed.

B. L. Hathorne, Chairman of the Sub-Committee on Rayon reported that his committee had spent considerable time in preparing a list of subjects which might be worked upon to advantage by any who were interested in research work in regard to rayon. This list will be published in the 1932 Year Book. It was also reported that this list had been forwarded to the Textile Foundation, and an offer had been made to that body to assist in any possible way in advancing research work upon any of these subjects, and also to act in an advisory capacity in connection with any work concerning rayon that might be undertaken by research fellows, working under the Textile Foundation.

Howard D. Clayton, Chairman of the Sub-Committee on Shrinkage of Textiles reported progress and also stated that the study of the shrinkage of textile materials to those composed of cotton would be studied in the near future.

The possibilities of preparing a list of textile chemicals, other than dyes, for publication in the Year Book was discussed but definite decision in this matter was deferred for future action.

In the absence of Hugh Christison. Chairman of the Sub-Committee on Fastness of Dyed Wool, Roland E. Derby reported that considerable work had been done in regard to changing some of the standards for the washing tests, and that this work would be completed in time for publication in the 1932 Year Book.

Respectfully submitted,

A. NEWTON GRAVES,
Secretary.

EIGHTY-FIRST MEETING, RESEARCH COMMITTEE

THE Eighty-first meeting of the Research Committee was held at the Chemists' Club, New York City, April 28th, 1933.

The following were present:

L. A. Olney, Chairman; Wm. H. Cady, Ralph F. Culver, Roland E. Derby, Carl Z. Draves, Ephraim Freedman, Walter E. Hadley, Jos. F. X. Harold, Ralph Hart, E. H. Killheffer, Frederick Krassner, Hans Meyer, Wm. R. Moorhouse, George A. Moran, Robert E. Rose, Raphael E. Rupp, Walter M. Scott, Walter S. Williams, A. Newton Graves.

The Chairman reported that several new sub-committees had been formed, among them one on "Vat Printing Pastes," of which Wm. H. Cady was chairman. Another on "Carbonizing" of which Roland E. Derby is chairman.

Reports in regard to the work of both of these committees were later presented by the respective chairmen.

Ralph Hart, Chairman of the Sub-Committee on Sulfonated Oils, reported concerning the work which was being done on the determination of SO_3 groups in sulfonated oils.

Frederick Krassner of the Naval Supply Depot in Brooklyn gave an interesting account of his work in connection with the shrinkage of textiles.

The possibilities of publishing in the 1933 Year Book a list of textile chemicals, other than dyes, which had already been discussed at the previous meeting was again considered. After considerable discussion it was voted to publish a list of such chemical as were of known chemical character, or constitution. The matter was to be left to the Year Book Committee. The chairman announced that two additional members of this committee would be appointed to specially take charge of this portion of the Year Book.

Respectfully submitted,

A. NEWTON GRAVES,
Secretary.

Proceedings of the American Association of Textile Chemists and Colorists

THE ENCHANTED ISLAND

BRING your children to Chicago's World's Fair, for this exposition has provided a five-acre land of make-believe where thousands of children may play in a story-book setting while their fathers and mothers are seeing the sights.

It is the Enchanted Island, the offical children's development located on Northerly Island between Lake Michigan and the Lagoon. Its attractions are numberless and whatever the age of the child it will be hard to draw him away from the Island though there are many other exhibits on the mainland equally enchanting.

There is a miniature railroad pulled by a modern combustion locomotive with a little train of cars on tracks that encircle the Enchanted Island passing many points of interest, including the large figures of Little Red Riding Hood, Mother Goose, Jack-and-the-Bean Stalk, the Old Lady who lived in a Shoe, the Three Bears and Jack and Jill. The train runs through a tunnel and skirts the rocks along Lake Michigan making stops at two miniature railroad stations. The lucky boy who is first to climb into the fireman's seat so that he can pull the bell all the way around has to deal with the competition of his father as well as the children for an observer notices that the parents do not always just leave the kids at the Island but often stay and play with them.

Artist's conception of the "Enchanted Island"—five-acre wonderland at A Century of Progress—Chicago's 1933 World's Fair, where parents may leave their children while attending other Exposition attractions. It has a Magic Mountain, a Tropical Garden, a Children's Theater, a miniature railroad, performing animals, a wading pool and other marvels.

A zoo and a model farm inhabited only by baby animals is another unusual attraction.

A Magic Mountain, 30 feet high, rises from the center of a circular court. It is surrounded by water with a bridge and some small boats to reach the mountain. The boats may sail the moat surrounding the mountain as they are side-wheelers propelled by boy or girl power. The water is only 30 inches deep. A winding path bordered by rocks and growing vegetation, and a sparkling brook lead to the summit where rises a Fairy Castle. From the peak of this Magic Mountain, the children enjoy a bird's eye view of the Enchanted Island. Youngsters who enter the castle shoot down a mysterious spiral slide to the base of the mountain.

Other enchanting features are a tropical garden with palm trees and orange trees bearing real fruit; a clipped pivot hedge forms a maze into which the children may wander and have fun trying to find the way out. There is a pirate's cave and a tree house built into the branches of trees.

There is no extra charge for admission and the Island has become the favorite spot in which to leave children because of its inclosure with a central entrance and exit and the fact that there are attendants there watching for lost children and caring for them until the parents show up. At the present time the loud speakers located all over the Fair Grounds have been announcing about once a minute that Johnny Green aged 10, has wandered off and if he will ask a guide to bring him to the Enchanted Island he will find his Uncle Dick there in front of the monkey cage.

The amusement devices in the form of concessions are moderate in price and an announcement has just been made that on Fridays they will be only five cents all over the grounds for the children. Those on the Island particularly designed to please youngsters are miniature drive yourself automobiles, a circular swing, miniature whip, fairyland ride, kiddy-go-round, pony cart ride, miniature ferris wheel and others. If your child is of the age when he thinks such amusements a little tame you will probably be asked to take him up in the dirigible, the sky-ride, the observation balloon and the Sikorsky amphibian.

This is but a brief account of the wonders of the Island and considering the hundreds of other things of interest to children and parents alike on the mainland you should try if possible to bring your children with you when you come to the Convention. They can spend the day there and can never be truly lost with the boy scouts and guides on the lookout for stray children and returning them by the minute to the meeting place in the Enchanted Island.

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—A. Newton Graves, Secretary, care Franklin Process Company, Providence, R. I.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

A-1

Education—Ph.B., Brown Univ. '27, P.G. at N. C. State (M.S. this June).

Experience—several years experience as an analytical and research chemist; private research work on sulfonated oils. Twenty-seven years old, married. Will supply references.

A-2

Education—B.T.C., Lowell Textile Institute, 1932; also course in shorthand and typing.

Experience—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, single.

A-3

Education—Graduate Pratt Institute, also attended Brooklyn Polytechnic.

Experience—12 years laboratory work with dyestuff company, also chemist with chemical company conducting manufacturing and research on sulfonated oils, soaps and specialties. Practical and laboratory experience in the manufacture of textile and leather specialties and starches. Married, 29 years old.

A-B-1

Experience—over twenty years' experience in the laboratories of various chemical manufacturers, four months' experience as second hand in dye house, familiar with all types of dyes and fibers. Thirty-nine years old. Will supply references.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-3

Education—Graduate in chemistry and dyeing of Textile School, Krefeld, Germany.

Experience—2 years plant chemist, handling vat, diazo, and direct fast colors on rayon; 3 years as dyer on piece goods, crepes and all mixtures of celanese, rayon and silk, pure dye and weighted. Age 27, single, will go anywhere. References.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-4

Experience—Overseer of cotton and rayon piece dyeing. Familiar with all machines and all classes of colors. Has knowledge of chemistry, was at one time demonstrator of chemistry and dyeing at Manchester (Eng.) Institute of Technology. Prefers N. E., N. Y., N. J., or Penn., but will go anywhere. Fifty-two years of age.

B-5

Experience—Nine years of yarn dyeing on rayon, silk, cotton, and novelty yarns with acid, direct, vat and naphthol colors. Experience in yarn printing, fastness tests and also on dyeing silk piece goods and rayon knit goods. Will go anywhere; references.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

D-1

Education—Graduate textile course, 1911, Georgia School of Tech.

Experience—Has had experience in all branches of the textile industry but chiefly in sales work. Was at one time in the dyestuff business and later in hosiery manufacturing. Prefers Middle Atlantic or southern states.

AMERICAN
DYESTUFF
REPORTER

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THE INDUSTRIAL RECOVERY ACT

THE Industrial Recovery Act, as passed last week, is "intended to provide jobs for the unemployed and inject new life into industry." The main features of the measure, as amended, are as follows:

It gives the President and his aides wide powers in the promotion of self-regulation of industry, under Federal supervision, as a means of curtailing over-production, raising wages, shortening hours and in this manner to increase prices and employment.

It further authorizes a $3,300,000,000 bond issue to finance the building of Federal, State, local and public-benefiting private projects to create new employment.

It empowers the President to work out codes of fair competition to be accepted by industry voluntarily, and provides him with further power to compel adoption of the codes and makes offenders liable to a $500 fine.

It provides the President with authority to license an industry so as to force unwilling minorities into line.

As can be seen from the above the outstanding element of the act is the broad grant of power which it gives to the President. The success or failure of it will depend upon the administration of this power. If the government control runs too much toward the autocratic, the plan will probably fail, if industry is given a free enough hand to its own initiative which is directed to the *best* in a social sense, the plan has a good chance of success.

The *Textile Organon* has an interesting viewpoint on the subject as shown in these paragraphs.

"Society then has challenged the industrialists. It says to them in effect, 'You have made a mess of it in your attempts to run our productive enterprises; you have made us work for the machine instead of making the machine work for us. You tell us that the minorities in your industries, and circumscribing laws, have made it impossible for you to do a good job. Very well, you take control of these minorities and we'll shelve the oppressing laws for your benefit. *Now* let's see what you'll do about it. And if you don't "deliver" in say two years time, then something more drastic, and much less optional for you, may have to be tried.'

"Personally we've always liked to take sportsmanlike challenges like this one. It's like a poker game where one has talked beforehand about his prowess and boldness in betting; now in the middle of the game, we've been told to make good, or in the vernacular, 'Put up or shut up.' For our part we're going to put up all we have. The stakes are too high now to welch, and besides, we love just such a game for what it is worth."

Robert L. Lund of St. Louis, president of the National Association of Manufacturers, an association which has shown objection to certain provisions in the original bill, has appealed to industry for the support of this act. He stated that the Recovery Act in its final form represents considerable improvement over the bill as it originally passed the House. He declared that while industry has urged adoption of certain safeguarding amendments, some of which were adopted, it has at all times been in sympathy with the declared objectives of the legislation. An important point that he brings out is that he believes that the administration of the measure will be in safe hands but to assure the success of the law requires the fullest cooperation.

In a statement released after the passage of the bill, Henry I. Harriman, president of the Chamber of Commerce of the United States, declared that the passage of the act was a most important step in progress toward rehabilitation of business. He further says:

"The act will permit American firms, determined to protect American standards of living, from being forced through cutthroat competition to lower standards. It will permit them successfully to meet unfair competition from unscrupulous minorities in their industries which has been carried on at the expense of large numbers of employes."

Such are some reactions to the passage of this bill. There are others that are just as strong in opposition to it. Perhaps the greatest objection is to the vesting of so much power in the hands of the President. Certain groups are in fear that he will use this too widely and endanger the chances of getting the proper co-operation from industry. Certain groups in the textile industry, for example, state that they will need a 40 hour week. In the event that the President decrees that 30 hours shall be the maximum, there will be considerable objection from this quarter.

However, the whole thing should be regarded more or less as an experiment or a challenge. If it works out successfully, it is probable that the two year limitation placed upon it will be automatically extended. There are so many contributing factors to the success or failure of the plan that it is too difficult to predict just what will be the ultimate result.

Textile Foundation News

Moth Insecticides

Evading the defense set up by several hundred "insecticides," clothes moths inflict an annual damage of $100,000,000, H. E. Ritchey, Textile Foundation Research Fellow, states. Some of the multitude of patented mothproofs are ineffective, he explains, but the chief loophole for moth attacks probably lies in defective conditions of application. Striking at the root of the problem, Mr. Ritchey is working at the University of Illinois under Dr. Roger Adams to determine the feasibility of developing fabrics with a "built-in" moth repellent.

"The housewife is conscientious in her effort to eradicate clothes moths, but circumstances conspire against her success," says Mr. Ritchey, in outlining the progress of his research to Franklin W. Hobbs, Chairman of the Foundation. "Sprays, for instance, are not applied thoroughly, or fumigants are allowed to escape through lack of air-tight chests or wardrobes. We are trying, therefore, to find a means of incorporating a moth repellent in fabrics during the course of their processing, thus to relieve the housewife of her tedious and too-often unsuccessful mothproofing endeavors.

"There are over six hundred mothproofing materials patented, not including fumigants," Mr. Ritchey asserts. "Some of the most commonly used substances are paradichlorobenzene, naphthalene, carbon bisulfide and carbon tetrachloride. Of the many materials, some seek to kill the moth, others endeavor to nauseate him and thus divert his presence or his appetite. Some methods probably only lighten the moth's daily routine.

"The great number of 'proofs' attests to the serious need for protection against moth ravages, and would seem to assure adequate defense. In actual practice, however, few of the materials prove entirely satisfactory. Some are inflammable, others poisonous to humans, some malodorous, others difficult to apply, and still others are unsatisfactory because of their expensiveness.

"To be ideal, mothproofing materials should first be effective, have no objectionable odor, should adhere evenly to the fabric treated, be unrecognizable on the material, not dust off, not be toxic to humans, and be reasonably priced.

"The habits of moths are their greatest protection," according to Mr. Ritchey. "They prefer dark places and are seldom seen in the light. The moth that seeks the bright lights and incites the housewife to frantic efforts is usually a harmless variety. His destructive brother works under cover and frequently goes undetected until the damage is discovered.

"Our research problem first is to determine some of the most nearly ideal moth repellents, then to discover the most practicable method of building such materials into fabrics. There is at present a green dye on the market that has this moth-repellent quality. Possibly a wide range of such dyes could be developed so as to give that method widespread mothproofing effectiveness. The critical question in such an attempt would be whether the combination of the repellent with the dye could be effected without interfering with their independent qualities."

Use of the X-Ray

The X-ray, friend of humanity through medical science, has been engaged in behalf of the textile and allied industries through the Textile Foundation. Textile manufacturers know the fabricating and processing qualities peculiar to cotton and other vegetable fibers, and the consumer is aware of their respective wearing qualities. But it is the idea of Wayne A. Sisson, Foundation Research Fellow, to employ the X-ray to determine why plant fibers behave as they do, and whether their properties can be improved.

"Our research is important to consumer, manufacturer and scientist alike," Mr. Sisson reports to Stuart W. Cramer, Director of the Foundation. "Tensile strength, resistance to wear, and ability to take and hold color depend upon the structure of textile fibers, hence our supermicroscopic scrutiny of plant fiber composition here at the University of Illinois." The work is progressing under the direction of Dr. George L. Clark, University of Illinois, and with the cooperation of Mrs. W. K. Farr, U. S. Department of Agriculture representative at Boyce Thompson Institute.

"We can examine the external structure of a cotton fiber under the microscope and find it to be composed of fibrils," Mr. Sisson continued. "We may also determine chemically that the elements present are carbon, hydrogen and oxygen, but we cannot observe these atoms visually. The nearest approach to this type of examination is by use of the X-ray. The X-ray is able to penetrate between the atoms and produce diffraction patterns which may be photographed, and from these we are able to deduce how nature arranges the atoms to build up the structure of cellulose.

"Using the Empire State building as an analogy, there is roughly the same relation in size between the building itself and the particles of sand and clay in one of its bricks, as that between a cotton fiber and the atoms of carbon, hydrogen and oxygen. In order to bridge this gap be-

(Continued on page 401)

Formaldehyde in the Treatment of Textile Materials

(Continued from page 381)

formalizing reaction it is of interest to consider the following data obtained by Wood. In the actual experiments purified cotton and viscose rayon yarn was humidified to various measured degrees (measured by drying at 105° C) by exposure to an atmosphere over aqueous sulfuric acid solutions of known concentration. They were then immersed at constant temperature in ten times their weight of a solution of hydrogen chloride in toluene containing 25% of formaldehyde (in its polymerized form of paraform) calculated on the weight of the cellulose. The reaction between the cellulose yarn and the paraformaldehyde was allowed to take place in stoppered glass bottles for various periods of time. The treated yarn was then washed in toluene, centrifuged, immersed in hot soda ash solution, and afterwards boiled with soap and ammonia until all traces of loosely adhering formaldehyde were removed.

Employing a 1% hydrogen chloride solution in toluene at 25° C. for 20 minutes the following results were obtained with ordinary cotton, mercerized cotton, and viscose rayon:—

Water content of reaction mixture	*Combined formaldehyde in treated yarn*	*Dyeing properties*
Ordinary cotton.		
2.0%	0.24%	Dyes
3.5	0.54	Resists dyes
5.0	1.09	Resists dyes
6.5	1.25	Resists dyes
9.5	1.42	Dyes
22.0	1.56	Dyes deeply
Cotton mercerized and driea at 105° C.		
1.2%	0.3 %	Dyes
3.7	0.64	Dyes
6.2	1.43	Dyes
7.2	1.87	Dyes
10.5	2.34	Dyes
20.0	2.2	Dyes deeply
Viscose rayon		
3.8%	0.35%	Resists
8.5	0.92	Dyes
10.4	1.07	Dyes
14.0	2.34	Dyes
17.7	2.64	Dyes
28.0	2.86	Dyes very deeply

In every instance it is noticed that the presence of water in the formalizing reaction mixture favors the production of a product which has increased dyeing properties; only in the case of mercerized cotton is a product which resists dyeing not obtained. Wood notes that it is really the amount of moisture present in the reaction mixture at the end of the reaction which determines whether or not the product resists dyes.

The acetylation of cotton is facilitated by a slight previous degradation of the cotton, but apparently such treatment does not assist in formalization as may be seen by comparing the following data with those tabulated above:

Water content of reaction mixture	*Combined formaldehyde in treated yarn*	*Dyeing properties*
1.0%	0.29%	Resists dyeing
3.2	0.65	Resists dyeing
4.8	1.53	Dyes
6.5	2.1	Dyes lightly
8.0	2.3	Dyes lightly
16.2	2.1	Dyes deeply

The cotton used in these experiments was first degraded by heating with 0.1 N. hydrochloric acid at 100° C. for 15 minutes.

It may at this stage be pointed out that when formalized cellulose is heated with aqueous hydrochloric acid the formaldehyde is split off; on this reaction is based a method for estimating the amount of formaldehyde combined with cellulose. In view of this fact it may be rightly concluded that complete formalization of a cellu-

lose fiber cannot be obtained by the method described above in which the cellulose is heated with toluene and formaldehyde in the presence of acid (hydrochloric acid). Wood has therefore attempted the formalization of viscose and cotton yarns with compounds containing the methylene grouping—CH_2O—capable of reacting in neutral or alkaline conditions. It is known that cellulose can be methylated under alkaline conditions with methyl sulfate as described by Denham (J. Chem. Soc., 1921, *119*, 80) and this method has proved particularly useful for preparing cellulose ethers. Hence the incentive to explore the possibility of using similar methods for formalizing cellulose fibers.

The chief substances containing the CH_2O group include the following:

Chloromethyl alcohol ..... $CH_2Cl.OH$
Mono-chloromethyl ether ..... $CH_2Cl.OCH_3$
Chloromethyl acetate ..... $CH_2Cl.O.COCH_3$
Di-chloromethyl ether ..... $(CH_2Cl)_2O$
Methylene sulfate ..... CH_2SO_4
Methylene disulfate ..... $CH_2(O.SO_3H)_2$
Di-chlorodimethyl sulfate ..... $(CH_2Cl)_2SO_4$
Chlormethoxysulphonyl chloride ..... $CH_2Cl.O.SO_2Cl$
Mono-chlorodimethyl sulfate ..... $CH_2Cl.O.SO_2.OCH_3$

and of these, Wood has found most useful to be dichlorodimethyl sulfate and chloromethoxysulfonyl chloride.

By means of these new formalizing (methylenating) agents it proved possible to prepare the mono-methylene ether of cellulose containing 17.2% and thus agreeing with the formula A, previously given. But it is by no means easy to introduce so much formaldehyde into the cellulose molecule and in order to attain the maximum combination of formaldehyde it is necessary to repeat the formalizing treatment several times. The following account of one method of formalizing highly a cellulose fiber is useful to those who wish to conduct further research along these lines.

Cotton sliver is soaked in caustic soda of 40° Tw., then centrifuged and dried in a desiccator until the moisture content is about 23%. Then 2.15 grams of this alkali-cellulose is boiled with 10 grams of dichlorodimethyl sulfate dissolved in 50 cc. of toluene. The product is found to contain 2.6% of combined formaldehyde.

A more effective formalizing treatment is further described by Wood who was in this manner able to secure combination of up to 17% of formaldehyde. In this method, cotton sliver is treated for five minutes with sulfuric acid of 140° Tw. containing 15% of paraform whereby a product containing 6.35% of combined formaldehyde is obtained. Apparently however much the composition of this acid-paraform mixture is varied it is not possible to secure combination of more than 7% of formaldehyde. The product is then further treated with caustic soda and dichlorodimethyl sulfate as previously described and in this manner the combined formaldehyde is increased by the first additional treatment to 10.7%, the third to 17.6%, the fourth to 17.5% and the sixth to 17.4%.

Chloromethoxysulphonyl chloride can be used in much the same manner and a similar product obtained.

Obviously in these reactions a considerable amount of moisture is present and it is probably for this reason that the formalized cotton which results has considerable affinity for moisture. The moisture absorptive properties of cotton fully formalized as described above and as recorded by Wood have been used to prepare the curve A in Fig. 3 in order that this may be compared with a similar curve B for untreated cotton as determined by Urquhart and Eckersall (J. Text. Inst., 1930, *21*, 500 T).

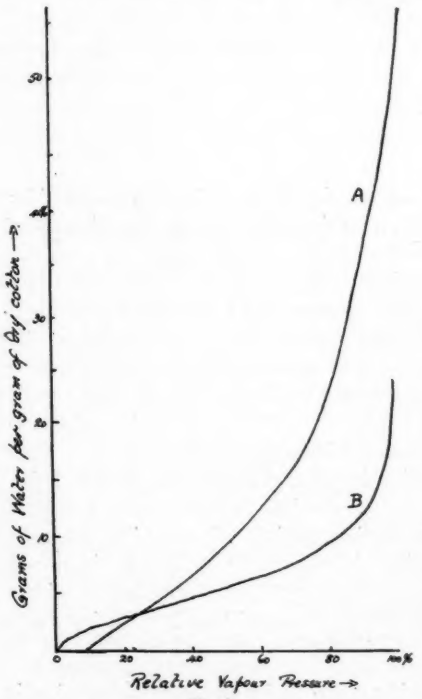

Fig. 3
A is moisture absorption curve for cellulose methylene ether
B is moisture absorption curve for cotton

Having indicated the manner in which cellulose fibers such as cotton and viscose rayon may be more or less converted into cellulose methylene ether by the action of formaldehyde or other product containing a methylene group it is now possible to consider something of the practical applications. In the first place it seems likely that, in view of the stability of cellulose methylene ether to caustic alkalis, formalized fibers could prove a valuable substitute for the cellulose ester fibers (for example, cellulose acetate) which are now important but which have so little resistance to saponification by even weak alkalis such as soda carbonate. It is true that the cellulose methylene ether is not so stable to hot acid liquors but on the whole it is much more important that it should be resistant to alkalis rather than acids. Again, by printing a formalizing mixture on cotton or viscose rayon fabric and then drying under suitable conditions there could be produced fabric capable of being dyed in two-tones or possibly two colors. But today there is a big demand for

methods for modifying the handle and luster of fabrics, and it is likely that much could be achieved in this direction by suitable formalizing treatments.

Recently it has been discovered that the formation of synthetic formaldehyde resins within cotton fibers leads to the production of a non-creasing product. But a synthetic resin of this type can be formed by combining formaldehyde with cellulose, and thus it may well happen that cotton and viscose rayon goods can be made non-creasable by such a reaction without the use of other compounds such as phenol and urea which are required in the methods at present in use (E. P. 291473 and 291474).

It is suggested that in the formalizing of cellulose fibers there is open a gateway to many opportunities for achieving new and useful effects.

RAYON DYEING AND FINISHING

(Continued from page 384)

The fabric is first passed over a spreader that removes wrinkles and stretches the fabric to the desired finished width. It then passes over a steaming apparatus that drives dry steam through the fabric. The object of the steam is twofold.

(1) To supply the necessary moisture.

(2) Softening the fabric before the rolling operation.

After steaming the fabric is continually passed through rollers where it is subjected to heavy pressure which temporarily sets the fabric and gives it a flat pleasing appearance.

The rollers may be either hot or cold according to the desire of the operator—cold rolls being generally preferred today.

After rolling, the fabric is passed over an air cooling device where it is cooled and at the same time vibrated slightly in order that it may become loose and thus be given a more pleasing hand.

The fabric is then continuously rolled upon a cardboard tube in which form it remains until cut into garments.

(To be continued)

TEXTILE FOUNDATION NEWS

(Continued from page 398)

tween the atoms and fibrils, and to study the larger groupings of the cellulose chains which are below the microscopic range of visibility, a new type of X-ray tube and camera is being developed which will give longer wave lengths than that used at present.

"The structure of cellulose is being studied indirectly by observing with X-rays the chemical changes produced by heat, oxidation and aging. From a botanical standpoint, the way in which nature builds up the cellulose in the cell walls of the fiber is being studied by making an X-ray and microscopic examination of the daily stages of growth in cotton fibers.

"A micro X-ray method for obtaining diffraction patterns from single fibers has been successfully developed, and thus enables the X-ray and microscopic structure of a definite section of a single fiber to be compared. A direct comparison is not possible by the usual method since it requires a bundle of about one hundred cotton fibers. We hope this X-ray and microscopic study may lead to a practical method for the scientific classification of various grades of cotton."

Wool Research

The interests of consumer, garment manufacturer, dyer and cleaner, and wool manufacturer alike are involved in research sponsored by the Textile Foundation on the fundamental characteristics of wool. This investigation, linked with the fulling, felting, dyeing, insulating, and the undesirable shrinkage property of wool, is being conducted by W. O. Teeters, Foundation Research Fellow, at the University of Illinois under Dr. R. L. Shriner.

"Many of the wool manufacturing processes and subsequent treatments of wool products are based on 'rule of thumb' methods rather than scientific facts," says Mr. Teeters in a report to Franklin W. Hobbs, Chairman of the Textile Foundation Board of Directors. "Certain of the peculiar and valuable properties of wool, particularly that of fulling, are sometimes attributed to the presence of a carbohydrate 'Elasticum'. Experiments prove, however, that wool contains no carbohydrate, so we must look elsewhere for the explanation of wool characteristics.

"The fulling of wool depends physically upon heat, moisture, friction and soap," Mr. Teeter states. "This is a unique property not possessed by cellulose fibers and causes an actual shortening and matting together of the fibers. The exact identity of the components involved will be of extreme assistance in obtaining a chemical explanation for the fulling property of wool.

"Another reason for the study of this component of wool is connected with the problem of cleaning woolen fabrics. There are two general methods whereby the dirt can be removed from the woolen clothes or blankets: (1) Washing with soap and water; (2) Dry cleaning. Each of the two methods have some disadvantages which cannot be overcome until more is known about the chemical properties of the wool fiber.

"Among the disadvantages of dry cleaning are the undesirable glossiness produced and brittle character that the fiber assumes after repeated cleansing. The cost and fire hazard are also objectionable. The washing of woolen clothes with soap and water causes them to shrink. Shrinking is merely a completion of the fulling process. Shrinkage of woolen goods causes considerable concern to the

housewife to say nothing of the actual weakening of each fiber if the soap and water bath is alkaline.

"The properties possessed by wool," we find, "depend upon the protein molecule, keratin, of which wool is composed. Therefore a thorough investigation of the chemical properties and structural orientation of this protein molecule is now under way. Answers to the questions: Why can wool be felted? Why is wool elastic? Why is wool a good insulator for heat? Why may dyestuffs be less liable to fade on wool and are faster on wool than any other fabric? Why is wool almost non-inflammable? and many other puzzling questions can be given only when more knowledge of the arrangement of the amino acids, which are the building stones for the keratin molecule is obtained.

"With this knowledge, methods and ways can be developed to protect the natural qualities of wool so the housewife will be able to wash her woolen clothing without fear of shrinkage or of injuring the fiber."

Physical Properties of Textile Fibers

The great strength and elasticity of silk in parachutes has contributed much to the safety and therefore the development of aeronautics. Wool bathing suits are popular because of their warmth and absorptive qualities. Similarly other common textile fibers enjoy peculiar properties which recommend them to the public. Science indicates that these differences are probably caused by the inherent structure of the fiber, but as this important matter lacks an adequate background of fact that Textile Foundation has instituted research to determine that exact relation and how the best qualities of fibers can be preserved or developed.

"The forms in which textiles may be produced have been multiplied many times, but as yet the fiber itself is somewhat of a mystery," reports G. Gordon Osborne, Foundation Research Fellow. "Science is now attempting to learn more about the various texile fibers—why and how they exhibit their respective characteristics," continued Mr. Osborne, who is engaged at Massachusetts Institute of Technology, under the direction of Dr. E. R. Schwarz, in a microscopic examination of both the external and internal characteristics of textile fibers.

"The investigation of the physical properties of textile fibers is a broad field," states Osborne's report made public recently by Frank D. Cheney, Director of the Textile Foundation. "It is a field in which little work has been done. What investigation has taken place has been abroad, mainly in Great Britain and Germany, but as yet the surface of the possibilities has scarcely been scratched.

"The work that is taking place at M.I.T. has for its broad purpose the application of scientific research of a fundamental nature to the inherent physical characteristics of textile fibers. The previous work will form the background and much valuable information can be drawn from it and used to advantage. However, the work in the past has centered mainly on obtaining information about the dimensional attributes of the fibers. Thus the information is largely concerning the gross micro-dimensions, in simple, the diameter, cross-sectional area, density, convolutions length and many others.

"Our work is to center more particularly on the details of external and internal fiber structure. In this respect the study is almost entirely new, what has been done before has been only incompletely pursued. The attempt will be to correlate the microscopically visible or detectable structure with chemical and X-ray analysis and with the results of physical tests as for strength, elasticity, elongation, etc. These other investigations are also being carried out under the auspices of the Textile Foundation.

"Further definite progress in textiles depends upon more specific knowledge of textile raw materials. Upon such knowledge will rest the adoption, improvement, and modification of present manufacturing methods and techniques. For with a more complete understanding of the reactions and workings, that is, the behavior, of the fibers, their advantages as well as their limitations will be better seen. Efforts now wasted will be conserved and the necessary work to be done will become more efficient."

1933 Graduates, A. French Textile School

At the Commencement exercises held June 5, fifteen students of the A. French Textile School, Georgia Tech, received B.S. degrees, and one an M.S. degree in Textile Engineering. The class also included two graduates in the five-year co-operative course.

Honors awarded to the members of this class were as follows: The medal of the National Association of Cotton Manufacturers, to A. D. Zellner, and the medal of the Cotton Manufacturers Association of Georgia, to J. A. Fife.

New Oil Products

The Quaker Chemical Products Corporation at Conshohocken, Pa., have applied for a patent on a new oil product that can be added to the following waxes: Paraffine Wax, Japan Wax, Carnauba Wax, Montan Wax, Ceresin Wax, and Ozokerite Wax for the purpose of making them water soluble. With some of the waxes the dispersion is so fine that there is no separation of the solid wax in long water dilutions.

This same material is also said to combine with fatty and mineral oils and also straight white mineral oil, making the finished combination completely soluble in water.

Article on Thallium

The Foote Mineral Co., 1609 Summer St., Philadelphia, have issued a copy of an original article on thallium by Dr. James C. Munch. Descriptions are given of the uses of thallium in pigments, catalysts and other chemical uses. Copies of the article may be obtained on request.

Commencement at Lowell Textile

The Thirty-Fifth Commencement of Lowell Textile Institute took place in Southwick Hall at the Institute on June 6th. The address of welcome was made by Charles E. Eames, president of the Institute. The presentation of the class fence ring to the class of 1934 was made by Henry A. Wells, president of the class of 1933.

Edwin S. Shaw, Department of Education, Tufts College, spoke on "Yesterday, Today and Tomorrow."

Graduates in Textile Chemistry and Dyeing Course—Standing, L. to R: Dempsey, Turcotte, Savard, Wells, Markarian, Robillard—Sitting, L. to R: Murphy, Pizzuto, Stearns, Young, Wojas.

The degree of Bachelor of Textile Chemistry was awarded to twelve students; the degree of Bachelor of Textile Engineering was awarded to four students; diplomas in Wool Manufacturing were awarded to two students and a diploma in Textile Design was awarded to one student.

Members of the graduating class who are also members of Tau Epsilon Sigma, scholastic honorary fraternity of the Institute, were as follows: Joseph J. Pizzuto, B.T.C., Gerald A. Robillard, B.T.C., Morris Lifland, B.T.E., and Theodore Recher, B.T.E.

Textile Courses at M. I. T.

Textile Microscopy, Textile Technical Analysis, and Textile Laboratory are the special summer courses being offered again this year by the Massachusetts Institute of Technology under the direction of Professor E. R. Schwarz. The work begins on July 26 and continues for six weeks ending on September 6.

Textile Microscopy consists of 30 lectures and 45 hours of laboratory. The lectures will be given at 10:15 each weekday except Saturday and the laboratory will be offered from 1:00 to 3:30 on Monday, Wednesday, and Friday afternoons.

Textile Technical Analysis consist of 30 lectures given on each weekday morning with the exception of Saturday from 9:15 to 10:15 and will cover the technique of the physical testing of textiles (exclusive of optical methods) and will also include discussion of methods of report writing, precision of measurements, graphical interpretation of data and the elements of fabric and yarn structure.

Textile Laboratory may be devoted to work in Textile Technical Analysis, to work in Textile Microscopy or both and is offered to fill a 15-hour per week schedule, arranged to suit the convenience of the student. Registration for the laboratory work is strictly limited and an early application is necessary to ensure membership in the group.

Excellent living facilities are available at very moderate cost in the new dormitory group. Reservations may be made at any time.

Groups aggregating 58 men from the industry have taken these courses during the regular school year and the opportunity afforded during the summer has always met with gratifying response in the past. At this particular time the sort of information obtainable would seem of particular value to the industry.

R. & H. Department Changes

Dr. E. A. Rykenboer has been appointed general manager of the R. & H. Chemicals Department of the du Pont Company to succeed Mr. C. K. Davis, who was recently elected president and general manager of the Remington Arms Company, Inc., and Mr. Milton Kutz has been appointed assistant general manager of the department to succeed Dr. Rykenboer.

Dr. Rykenboer held important positions in the Roessler & Hasslacher Chemical Company before it was taken over by the du Pont Company. He was first general superintendent and later vice-president of that company. Since the R. & H. Chemicals Department was created in the du Pont Company, he has been assistant general manager.

Mr. Kutz, who becomes assistant general manager of the R. & H. Chemicals Department, has had a wide experience also in the Roessler & Hasslacher Chemical Company. He was successively branch office manager, general sales manager, and vice-president and manager of sales in that organization. Since the formation of the R. & H. Chemicals Department in the du Pont Company, he has been director of sales.

Dyes for Cotton Viscose Fabrics

Sample card No. 987 of the Society of Chemical Industry in Basle, *Direct and Chlorantine Fast Dyes on Cotton-Viscose Fabrics.* contains 100 dyeings on a patterned Cotton-Viscose weave in self shades and combinations. The dyestuffs illustrated are a selection of Direct and Chlorantine Fast dyestuffs which are especially suitable for this purpose. The Chlorantine Fast Colors are said to stand out pre-eminently over ordinary direct dyestuffs on account of their better fastness to light. The Chloranine Fast Dyes with best light-fastness are designated by the letters LL. All remaining Chlorantines are claimed to be notably light-fast and still much better than ordinary direct dyes.

1933 Fall Silk Colors

In the new collection of fall silk colors recently released by the Textile Color Card Association to its members, metallic tones of green strike a high fashion note, as expressed in Bronze Green and its lighter complement, Brass-green.

This season, the Association has issued the confidential advance card in an entirely different form. Instead of the ribbon samples of past seasons, the colors are portrayed in a piece-dye fabric and grouped in three series of loose-leaf swatches of generous size. This method is expected to prove especially practical for dyers and greatly facilitate the matching of shades.

In the interests of sound merchandising, fewer colors have been presented. There are sixty in all and a number of the oustanding basic shades are identical with tones appearing in the recently issued woolen card and have the same names.

Strong fashion interest is focused upon the brown family, especially warm shades with a hint of red, including Chona Brown. Liqueur Brown, a reddish tobacco hue, is likewise decidedly new in feeling and blends smartly with its lighter harmonizing tone, Spice Rose.

Textile Color Card Association Scholarships

Edward William Croner has been awarded the scholarship established by the Textile Color Card Association at the Philadelphia Textile School for the coming academic year, it was announced by Dr. E. W. France, director of the school, at the Commencement Exercises held recently.

Mr. Croner, who will be a member of next year's senior class, receives the award because of his particular aptitude along the lines of color and his general high scholastic standing. His tuition will be paid for the senior year, according to the terms of the scholarship. He will be required to present a thesis on color upon graduation. Sydney Lewine, of this year's graduating class, was the holder of the Association's scholarship at the Philadelphia Textile School during the past year.

Four years ago, the Textile Color Card Association established annual scholarships at the Philadelphia Textile School, the New York Textile High School and the Lowell Textile Institute. The winners of the scholarships at the two last named schools for the coming year will be announced later.

NEW PATENTS

(*Abstracted by S.O.C.M.A.*)

Production of (Brown) Vat Dyestuffs of the Dibenzanthrone Series. (A division of application serial No. 221,396, filed Sept. 22, 1927, U. S. Patent No. 1,742,317, dated Jan. 7, 1930.) Paul Nawiasky, of Ludwigshafen-on-the-Rhine, and Julius Mueller, of Mannheim, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,902,883, Mar. 28, 1933.

Trisazo Dye. (Prepared by coupling tetrazotized benzidine with 1.8-aminonaphthol-3.6-disulfonic acid (H acid), then coupling diazotized 1-naphthylamine-6 (or 7)-sulfonic acid (Cleve's acid), and finally coupling with 2.8-aminonaphthol-6-sulfonic acid; dye cotton from a neutral or slightly alkaline bath gray to blue-black shades of excellent fastness to light and to washing.) Frithjof Zwilgmeyer, of Hamburg, N. Y., assignor to National Aniline & Chemical Co., Inc., of N. Y., N. Y., No. 1,903,021, Mar. 28, 1933.

Process of Making Nitrogenous Vat Dyestuffs of the Acridine Series. (For example, comprises treating bz 1-benzanthronyl-1-amino-5-amino-anthraquinone with an alcoholic caustic potash solution, under reflux in the presence of anhydrous sodium acetate and cuprous chloride with tetrabromo-benzene in nitrobenzene; dye vegetable fiber gray shades of good fastness particularly to light and exposure.) Ernst Honold, of Frankfort-on-the-Main-Fechenheim, and Georg Boehner, of Friedrichsfeld in Baden, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,903,181, Mar. 28, 1933.

Monoazodyestuffs. (For example, comprises coupling aniline-2.5-di-sulfonic acid with 2-amino-8-hydroxynaphthalene-6-sulfo-N-methylanilide; dye wool clear red to black shades fast to light, likewise suitable for the manufacture of pigments and for printing; also suitable in dyeing cellulose acetate silk.) Hugo Schweitzer, of Leverkusen-Wiesdorf, Ger., assignor to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,903,599, Apr. 11, 1933.

Azo Dyestuffs. (Obtainable by coupling in aqueous alkaline solution a diazotized amino-sulfonic acid of the benzene or naphthalene series with a 1-naphthol-3.6- or 3.7-disulfonic acid amide or an N-alkyl or phenyl substitution product thereof; dye wool from an acid bath clear red to blue shades fast to light, washing and fulling; also suitable for the manufacture of color lakes and for printing.) Hugo Schweitzer, of Leverkusen-Wiesdorf, Ger., assignor to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,903,600, April 11, 1933.

Process for Manufacturing Vat Dyestuffs of the Perylene Series. (Whereby the chloride of perylene 3.9 dicarboxylic acid is condensed with amino quinones of the anthracene or perylene series; dye cotton in light yellow to full brown colors.) Alfred Pongratz and Alois Zinke, of Graz, Austria, assignors to Felice Bensa, of Genoa, Italy, No. 1,903,708, April 11, 1933.

Technical Notes From Foreign Sources

Present Condition of Our Knowledge of Oils, Especially of the Drying Oils

Dr. Kronsbein—Der Farben-Chemiker 3,373 (1932).—The behavior of the drying oils and the facts underlying the process of drying has formed a subject of investigation since any natural products have been investigated; that is, from the very beginning of modern chemistry. From the practical side, the process of drying would appear to be of interest only to the paint and lacquer industry; but today it has so much interest and importance to the finisher of artificial silks, and to the dyer who has to struggle with such finishing agents, that some comment upon the present article seems deserved.

Of course, there have been different explanations of the process of drying, and various hypotheses have been constructed for the purpose of bolstering up these explanations. E.g., Mulder has assumed that, in the process of drying, the glyceryl residue is oxidized away. It is now known that the glyceryl esters of the unsaturated fatty acids display a capability of drying great enough to be of some importance in the paint and lacquer industry, a capability wholly lacking in the ethyl esters, for example, of such acids. Another hypothesis, or a group of them, is based upon the possibility of an auto-oxidation of polymerization, or both, taking place during the drying. It is perfectly true that, in the drying, oxygen is absorbed and a peroxide formation takes place, but little more can be said. Auer's hypothesis, which naturally, in these days, seeks to involve the topic of colloid chemistry, quite evidently has gone too far in assuming a coagulating action of air in contact with the oil. He assumes too much, since he presupposes the colloidal condition to exist in the fresh oil, without examining the facts.

It would seem superfluous to point out that any really rational study must involve chemical and stereochemical, as well as colloido-chemical, considerations. This is the viewpoint of Scheiber and of Eibner, to whom we owe perhaps the most important contributions yet made to the subject.

According to the work of these two authors, the oils may be divided into three classes;

1—Triglycerides of multiply unsaturated fatty acids with conjugated double bonds; wood oil, which contains almost nothing except elaeostearic acid as its base, comes under this class.

2—Triglycerides of multiply unsaturated fatty acids, with isolated double bonds. In this class is linseed oil, a mixed-acid glyceride, containing principally linolenic acid (with three unsaturated linkages), and linolic acid (with two). Poppy oil also comes in this group.

3—Triglycerides of simply unsaturated fatty acids. In this group come almond oil (mostly involving oleic acid) and olive oil.

The typical oils of these groups display certain differences in their structure, and differences in their behavior as to drying. Wood oil dries excellently, linseed oil well, poppy oil much more poorly, while the members of group 3 practically do not dry at all. It would seem justifiable, in view of the simple parallelism of condition of unsaturation and behavior as to drying, to suppose that the structural condition is the cause of the behavior of the oil in the drying process; in fact, logic would compel this conclusion.

The physico-chemical side of the question has been carefully looked into. It was of importance to know positively whether the fresh oil is of colloid nature, or whether this condition is set up only when film formation begins. It has been proved experimentally that, in the fresh condition, a drying oil is not colloidal in nature. Wood oil yields up to 75 per cent of crystallized elaeostearine, the alpha form, which on exposure to light passes over to the beta form. From linseed oil crystalline bromine-addition products of the glyceride can be obtained. Measurement of the depolarization of fresh linseed oil, and of oil exposed to air at the ordinary and at higher temperatures, gives no evidence of alteration characteristic of colloids. The determination of viscosity shows no anomalies, and ultramicroscopic study also gives negative results.

As to what takes place during the drying process, there are various phenomena which indicate that the oil is passing into the colloidal state as it dries. E. g., layers of wood oil and of linseed oil do not dry from surface to substratum in uniform progression, but the drying proceeds gradually inward, with formation of a film upon the surface; while poppy oil dries uniformly through the whole layer, without the formation of a film. If a purely chemical explanation of the process were to be given, we should have to suppose that wood oil, which is chehically a simple substance, and contains no variable factors to speak of, should dry through uniformly, as does poppy oil. But, considered from the physico-chemical standpoint, there apparently forms first upon the surface a low-disperse colloid phase, which thickens into a film, and so prevents a uniform drying throughout the film. In the case of poppy oil, the transformation into the colloid state takes place so slowly, and in so slight a degree, that it never passes over to the film condition. However, in the formation of the film, purely chemical reactions are also at work; so that the chemical structure of the oil in question does have a determining influence upon the drying process. As the above chemical classification of the oils, given above, indi-

cates, there is a decided difference in the nature of the drying process, and conclusions drawn from the behavior of wood oil (conjugated double bonds) can properly not be applied to the case of linseed oil (where only isolated double bonds exist).

Any film formation may be considered to pass from the phase of initial drying, through that of apparent complete drying, to that of actual complete drying. The time required for passage from phase to phase varies with the chemical constitution of the oil under consideration. With wood oil and linseed oil, the stage of initial drying is recognized by the formation of a film, and by the increasing tackiness of the layer. At this point, only a small portion of the oil has passed into the colloidal state. The film then begins to dry from the surface inward, and passes through the stage of apparent dryness, which in some cases may lead to a resoftening of the surface, as the internal higher-disperse phase penetrates through the film to the surface again. Such a progressive alteration is greatly favored, e. g., by direct sunlight. After this intermediate phase has been passed through, the last one sets in. We have no means, as yet, of telling whether this phase, of complete drying, is complete, since apparently, at any recognizable point of apparently complete drying, an oxidative degradation of the substance will already have set in. For the paint and lacquer industry, it is of course important to know whether the "reaction" is a reversible one; that is, whether the film is or is not really insoluble in oils or such media (i. e., whether the first coat is sufficiently dry to allow a second coat to be applied without the first coat being softened and smeared up by application of the second one). This point will have been reached when the film is no longer fusible, but chars when heated sufficiently. Then, the high-disperse phase will have shrunk to the minimum.—For all these phenomena we have no purely chemical viewpoints, even though we recognize that constitutional degradation of the molecule, often so valuable in unraveling the sequence of reaction, is involved.

A serious gap in our knowledge exists in the matter of geometrical isomers—whether or not they exist, or are formed, in the oil. Linolic acid may theoretically exist in four, linolenic acid in eight, stereoisomeric forms. But by addition of bromine to the double bonds we always get only one of the isomeric forms of that derivative which ought to be possible. This gap in our knowledge is a profound one.

It has long been known positively that linseed oil takes up oxygen while drying. Mulder assumed the formation of true oxyglycerides or their anhydrides to take place. Eibner, however, has shown that these true oxy-acid derivatives do not form if the linolenic acid derivative is already initially oxidized; but that peculiar oxynic acids result instead. Fahrion was the first to suggest that, in the taking up of oxygen, a peroxide formation took place on the double bonds, these peroxide groups passing rapidly to the ketone form. If this view were correct, such ketone-acids must give, on reduction, true hydroxy-acids, but this does not take place. Accordingly, Marcusson concluded that the peroxide groups (he assumed that such groups did form) reacted with still intact double bonds of a second molecule to form 1-4-dioxane rings, which led, of course, to the idea of polymerization being a subsequent step involved.

Much has been published regarding the question of whether, in the formation of the film, auto-oxidation or polymerization, or both together, occur. Little light has come from that phase of the study, for no attention was given to the distinction in the drying process which is displayed by wood and by liseed oils; and the same concepts were regarded as valid for fresh oils and for those in which the drying process had been initiated by heating. When Boeseken and Ravenzwaay determined the existence of conjugated double bonds in wood oil, and the difference in behavior of films formed by fresh oil and by boiled oil, a decided step forward had been taken. Eibner discovered that films of fresh wood and linseed oils, on being preserved in closed containers for a year, went completely to pieces, while films from boiled oils remained unaltered during nine years—which at once indicated a decisive difference to exist between the two states of the oils.

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